

Connecting via Winsock to STN

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LOGINID:sssptal62lcon

PASSWORD:

TERMINAL (ENTER 1, 2, 3, OR ?):2

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NEWS 1 Web Page for STN Seminar Schedule - N. America  
NEWS 2 JAN 02 STN pricing information for 2008 now available  
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prophetic substances  
NEWS 4 JAN 28 USPATFULL, USPAT2, and USPATOLD enhanced with new  
custom IPC display formats  
NEWS 5 JAN 28 MARPAT searching enhanced  
NEWS 6 JAN 28 USGENE now provides USPTO sequence data within 3 days  
of publication  
NEWS 7 JAN 28 TOXCENTER enhanced with reloaded MEDLINE segment  
NEWS 8 JAN 28 MEDLINE and LMEDLINE reloaded with enhancements  
NEWS 9 FEB 08 STN Express, Version 8.3, now available  
NEWS 10 FEB 20 PCI now available as a replacement to DPCI  
NEWS 11 FEB.25 IFIREF reloaded with enhancements  
NEWS 12 FEB 25 IMSPRODUCT reloaded with enhancements  
NEWS 13 FEB 29 WPINDEX/WPIDS/WPIX enhanced with ECLA and current  
U.S. National Patent Classification  
NEWS 14 MAR 31 IFICDB, IFIPAT, and IFIUDB enhanced with new custom  
IPC display formats  
NEWS 15 MAR 31 CAS REGISTRY enhanced with additional experimental  
spectra  
NEWS 16 MAR 31 CA/CAPLUS and CASREACT patent number format for U.S.  
applications updated  
NEWS 17 MAR 31 LPCI now available as a replacement to LDPCI  
NEWS 18 MAR 31 EMBASE, EMBAL, and LEMBASE reloaded with enhancements  
NEWS 19 APR 04 STN AnaVist, Version 1, to be discontinued  
NEWS 20 APR 15 WPIDS, WPINDEX, and WPIX enhanced with new  
predefined hit display formats

NEWS EXPRESS FEBRUARY 08 CURRENT WINDOWS VERSION IS V8.3,  
AND CURRENT DISCOVER FILE IS DATED 20 FEBRUARY 2008

NEWS HOURS STN Operating Hours Plus Help Desk Availability  
NEWS LOGIN Welcome Banner and News Items  
NEWS IPC8 For general information regarding STN implementation of IPC 8

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\* \* \* \* \* STN Columbus \* \* \* \* \*

FILE 'HOME' ENTERED AT 07:16:56 ON 25 APR 2008

=> FILE REG  
COST IN U.S. DOLLARS  
FULL ESTIMATED COST

SINCE FILE ENTRY	TOTAL SESSION
0.21	0.21

FILE 'REGISTRY' ENTERED AT 07:17:31 ON 25 APR 2008  
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STRUCTURE FILE UPDATES: 23 APR 2008 HIGHEST RN 1016892-81-1  
DICTIONARY FILE UPDATES: 23 APR 2008 HIGHEST RN 1016892-81-1

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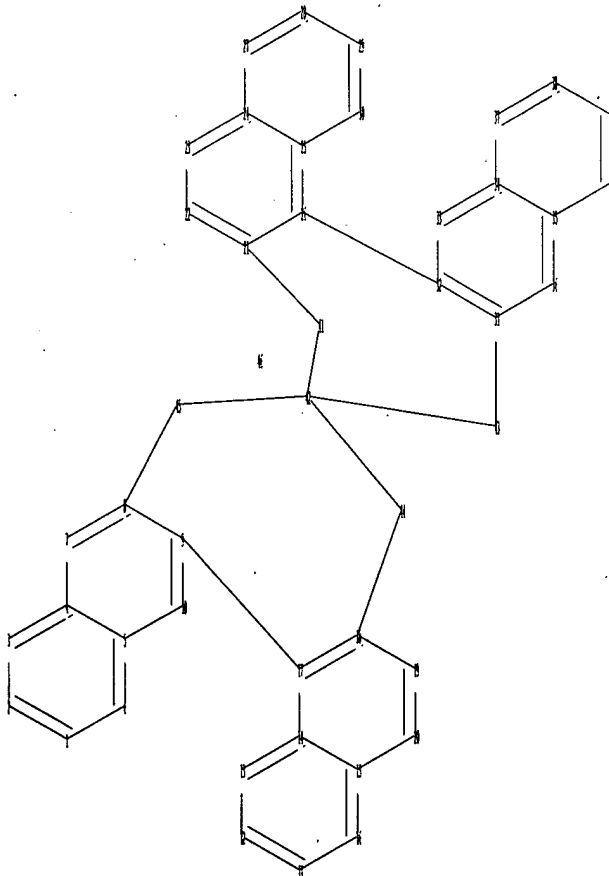
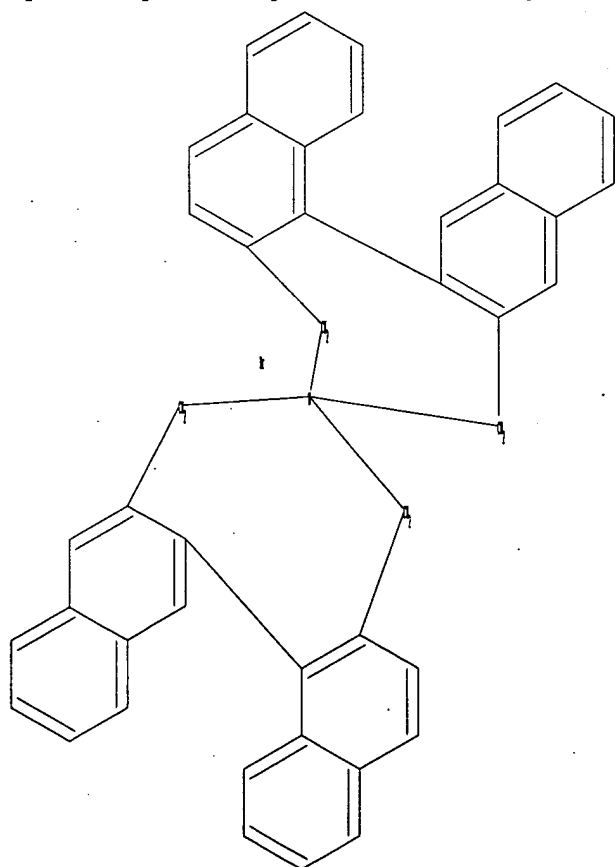
TSCA INFORMATION NOW CURRENT THROUGH January 9, 2008.

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<http://www.cas.org/support/stngen/stndoc/properties.html>

=>  
Uploading C:\Program Files\Stnexp\Queries\BBC-2.str



chain nodes :

46

ring nodes :

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23  
24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44  
45

ring bonds :

1-2 1-6 2-3 3-4 4-5 4-7 5-6 5-10 7-8 8-9 8-45 9-10 9-17 11-12 11-16  
12-13 13-14 14-15 14-17 15-16 15-20 17-18 18-19 18-44 19-20 21-22 21-26  
21-41 22-23 23-24 24-25 24-27 25-26 25-30 26-32 27-28 28-29 29-30 31-32  
31-36 31-43 32-33 33-34 34-35 34-37 35-36 35-40 37-38 38-39 39-40 41-42  
42-43 42-44 42-45

exact/norm bonds :

8-45 9-17 18-44 21-41 26-32 31-43 41-42 42-43 42-44 42-45

normalized bonds :

1-2 1-6 2-3 3-4 4-5 4-7 5-6 5-10 7-8 8-9 9-10 11-12 11-16 12-13 13-14  
14-15 14-17 15-16 15-20 17-18 18-19 19-20 21-22 21-26 22-23 23-24 24-25  
24-27 25-26 25-30 27-28 28-29 29-30 31-32 31-36 32-33 33-34 34-35 34-37  
35-36 35-40 37-38 38-39 39-40

Match level :

1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:Atom 8:Atom 9:Atom 10:Atom  
11:Atom 12:Atom 13:Atom 14:Atom 15:Atom 16:Atom 17:Atom 18:Atom 19:Atom  
20:Atom 21:Atom 22:Atom 23:Atom 24:Atom 25:Atom 26:Atom 27:Atom 28:Atom  
29:Atom 30:Atom 31:Atom 32:Atom 33:Atom 34:Atom 35:Atom 36:Atom 37:Atom  
38:Atom 39:Atom 40:Atom 41:CLASS 42:CLASS 43:CLASS 44:CLASS 45:CLASS  
46:CLASS

L1 STRUCTURE UPLOADED

=> D L1

L1 HAS NO ANSWERS

L1 STR

\* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT \*

Structure attributes must be viewed using STN Express query preparation.

=> S L1 FULL

FULL SEARCH INITIATED 07:18:02 FILE 'REGISTRY'

FULL SCREEN SEARCH COMPLETED - 457 TO ITERATE

100.0% PROCESSED 457 ITERATIONS

0 ANSWERS

SEARCH TIME: 00.00.01

L2 0 SEA SSS FUL L1

=> FILE CAPLUS

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

178.36

178.57

FILE 'CAPLUS' ENTERED AT 07:18:17 ON 25 APR 2008

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FILE LAST UPDATED: 24 Apr 2008 (20080424/ED)

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=> S L2  
L3 0 L2

=>

---Logging off of STN---

=>  
Executing the logoff script...

=> LOG Y

COST IN U.S. DOLLARS	SINCE FILE	TOTAL
FULL ESTIMATED COST	ENTRY	SESSION
	0.48	179.05

STN INTERNATIONAL LOGOFF AT 07:18:32 ON 25 APR 2008

Connecting via Winsock to STN

Welcome to STN International! Enter x:x

LOGINID:sssptal621con

PASSWORD:

TERMINAL (ENTER 1, 2, 3, OR ?):2

\* \* \* \* \* Welcome to STN International \* \* \* \* \*

NEWS	1		Web Page for STN Seminar Schedule - N. America
NEWS	2	JAN 02	STN pricing information for 2008 now available
NEWS	3	JAN 16	CAS patent coverage enhanced to include exemplified prophetic substances
NEWS	4	JAN 28	USPATFULL, USPAT2, and USPATOLD enhanced with new custom IPC display formats
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NEWS	8	JAN 28	MEDLINE and LMEDLINE reloaded with enhancements
NEWS	9	FEB 08	STN Express, Version 8.3, now available
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NEWS	11	FEB 25	IFIREF reloaded with enhancements
NEWS	12	FEB 25	IMSPRODUCT reloaded with enhancements
NEWS	13	FEB 29	WPINDEX/WPIDS/WPIX enhanced with ECLA and current U.S. National Patent Classification
NEWS	14	MAR 31	IFICDB, IFIPAT, and IFIUDB enhanced with new custom IPC display formats
NEWS	15	MAR 31	CAS REGISTRY enhanced with additional experimental spectra
NEWS	16	MAR 31	CA/CAPplus and CASREACT patent number format for U.S. applications updated
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NEWS EXPRESS FEBRUARY 08 CURRENT WINDOWS VERSION IS V8.3,  
AND CURRENT DISCOVER FILE IS DATED 20 FEBRUARY 2008

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FILE 'HOME' ENTERED AT 07:24:42 ON 25 APR 2008

=> FILE REG  
COST IN U.S. DOLLARS  
FULL ESTIMATED COST

SINCE FILE ENTRY	TOTAL SESSION
0.21	0.21

FILE 'REGISTRY' ENTERED AT 07:25:03 ON 25 APR 2008  
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DICTIONARY FILE UPDATES: 23 APR 2008 HIGHEST RN 1016892-81-1

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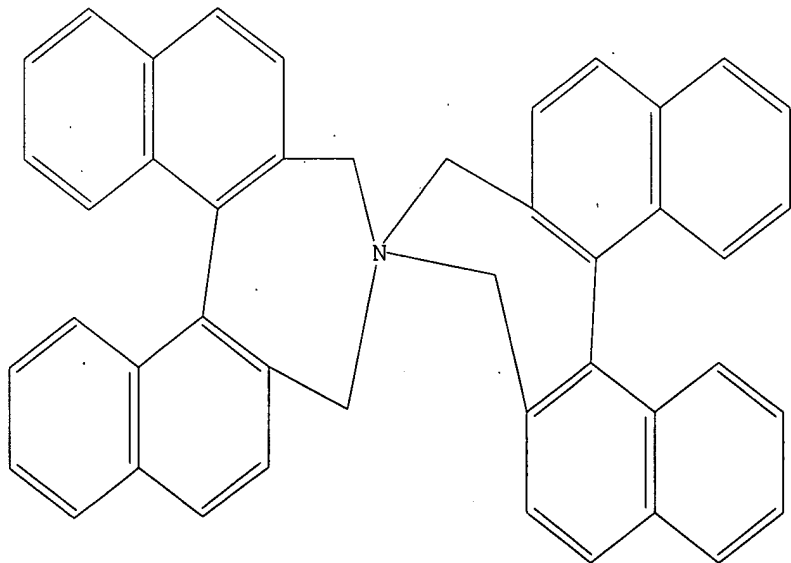
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<http://www.cas.org/support/stngen/stndoc/properties.html>

=>  
Uploading C:\Program Files\Stnexp\Queries\BBC-3.str

L1 STRUCTURE UPLOADED

=> D L1  
L1 HAS NO ANSWERS  
L1 STR



Structure attributes must be viewed using STN Express query preparation.

=> S L1 FULL  
FULL SEARCH INITIATED 07:25:46 FILE 'REGISTRY'  
FULL SCREEN SEARCH COMPLETED - 457 TO ITERATE

100.0% PROCESSED 457 ITERATIONS 131 ANSWERS  
SEARCH TIME: 00.00.01

L2 131 SEA SSS FUL L1

=> FILE CAPLUS  
COST IN U.S. DOLLARS SINCE FILE ENTRY TOTAL SESSION  
FULL ESTIMATED COST 178.82 179.03

FILE 'CAPLUS' ENTERED AT 07:25:59 ON 25 APR 2008  
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FILE LAST UPDATED: 24 Apr 2008 (20080424/ED)

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=> S L2  
L3 80 L2

=> D L3 IBIB ABS HITSTR 1-80

L3 ANSWER 1 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
ACCESSION NUMBER: 2008:63886 CAPLUS  
DOCUMENT NUMBER: 148:168969  
TITLE: Preparation of chiral halogenated phenylalanines from tertiary-butyl 2-diphenyliminoacetate using chiral spiro quaternary ammonium salt phase transfer catalysts  
INVENTOR(S): Kagawa, Takumi  
PATENT ASSIGNEE(S): Tosoh Corp., Japan  
SOURCE: Jpn. Kokai Tokkyo Koho, 14pp.  
CODEN: JKXXAF  
DOCUMENT TYPE: Patent  
LANGUAGE: Japanese  
FAMILY ACC. NUM. COUNT: 1  
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 2008007461	A	20080117	JP 2006-179753	20060629
PRIORITY APPLN. INFO.:			JP 2006-179753	20060629

OTHER SOURCE(S): MARPAT 148:168969

AB (R)-RC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH(NH<sub>2</sub>)CO<sub>2</sub>H [(R)-I; R = halo, C1-4 haloalkyl] are prepared by asym. benzylation of Ph<sub>2</sub>C:NCH<sub>2</sub>CO<sub>2</sub>CMe<sub>2</sub> (II) with RC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Br (R = same as above) in the presence of bis[[(S)-1,1'-bi[4,6-bis(octyldimethylsilyl)naphthyl]]-2,2'-dimethyl]ammonium bromide [(S)-III] and alkalis, and hydrolysis of the resulting (R)-Ph<sub>2</sub>C:NCH(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>R)CO<sub>2</sub>CMe<sub>2</sub> (R = same as above) with acids. Similarly, (S)-I are prepared by the above process using (R)-III. Thus, II was treated with 2-FC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Br in the presence of (S)-III and KOH to give >99% (R)-Ph<sub>2</sub>C:NCHYCO<sub>2</sub>CMe<sub>2</sub> (Y = 2-FC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>) with 98.5 %ee, which was hydrolyzed with HCl to give 85% (R)-o-FC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH(NH<sub>2</sub>)CO<sub>2</sub>H.

IT 832745-40-1 1001921-20-5

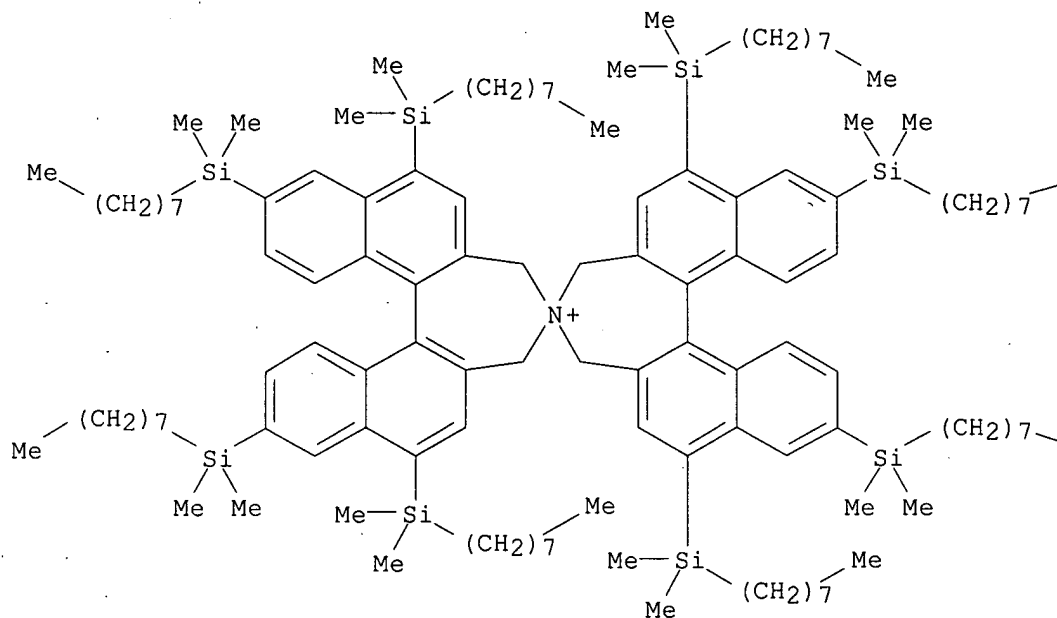
RL: CAT (Catalyst use); USES (Uses)

(preparation of chiral halogenated phenylalanines by benzylation of tert-Bu diphenyliminoacetate with chiral spiro phase transfer catalysts and alkalis, and hydrolysis with acids)

RN 832745-40-1 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 1,1',7,7',9,9',14,14'-octakis(dimethyloctylsilyl)-3,3',5,5'-tetrahydro-, bromide (1:1), (11bR,11'bR)- (CA INDEX NAME)

PAGE 1-A





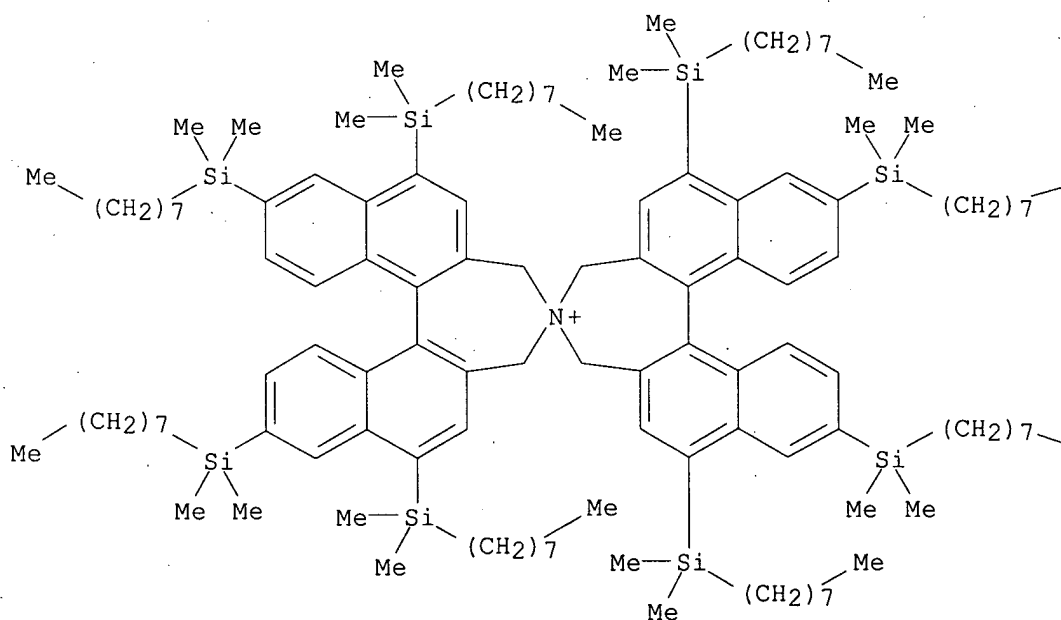
Me

● Br<sup>-</sup>

Me

RN 1001921-20-5 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 1,1',7,7',9,9',14,14'-  
 octakis(dimethyloctylsilyl)-3,3',5,5'-tetrahydro-, bromide (1:1),  
 (11bS,11'bS)- (CA INDEX NAME)

PAGE 1-A



Me

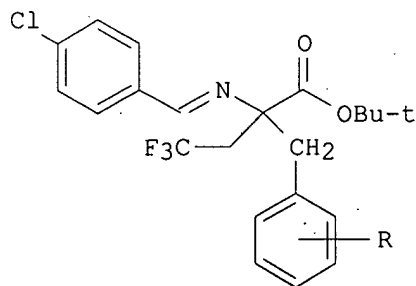
● Br<sup>-</sup>

Me

L3 ANSWER 2 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2008:63876 CAPLUS  
 DOCUMENT NUMBER: 148:168968  
 TITLE: Preparation of optically-active  $\alpha$ -(trifluoroethyl)phenylalanine derivatives and their intermediates  
 INVENTOR(S): Kagawa, Takumi  
 PATENT ASSIGNEE(S): Tosoh Corp., Japan  
 SOURCE: Jpn. Kokai Tokkyo Koho, 32pp.  
 CODEN: JKXXAF  
 DOCUMENT TYPE: Patent  
 LANGUAGE: Japanese  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 2008007460	A	20080117	JP 2006-179752	20060629
PRIORITY APPLN. INFO.:			JP 2006-179752	20060629
OTHER SOURCE(S):	MARPAT	148:168968		

GI



II

AB (R)- or (S)-RC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C(NH<sub>2</sub>)(CH<sub>2</sub>CF<sub>3</sub>)CO<sub>2</sub>CMe<sub>3</sub> [I; R = C<sub>1</sub>-10 (halo)alkyl, c<sub>1</sub>-10 alkoxy, H, halo], useful as intermediates for drugs, are prepared by hydrolyzing (R)-II or (S)-II (R = same as above), resp., in the presence of acids. (S)-II or (R)-II are prepared by reacting 4-ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NCH(CH<sub>2</sub>CF<sub>3</sub>)CO<sub>2</sub>CMe<sub>3</sub> (III) with RC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Br (R = same as above) in the presence of chiral phase-transfer catalyst spirobis[[(S)-1,1'-bi[4,6-bis(octyldimethylsilyl)naphthyl]]-2,2'-dimethyl]ammonium bromide (IV) or

its stereoisomer and alkalis. III is prepared by reacting 4-ClC<sub>6</sub>H<sub>4</sub>CH:NCH<sub>2</sub>CO<sub>2</sub>CMe<sub>3</sub> (V) with Li isopropylamide and then CF<sub>3</sub>CH<sub>2</sub>I. Thus, a THF solution of V (preparation given) was added dropwise to THF solution of

Li

isopropylamide at -80° over 30 min, the reaction mixture was stirred at -80° for 30 min, CF<sub>3</sub>CH<sub>2</sub>I was added dropwise over 10 min, the mixture was stirred at -80° for 30 min, gradually heated to room temperature over 2 h, and stirred at room temperature for 12 h to give 95%

III. A

mixture of III, spirobis[[(S)-1,1'-bi[4,6-bis(octyldimethylsilyl)naphthyl]]-2,2'-dimethyl]ammonium bromide, toluene, PhCH<sub>2</sub>Br, and CsOH was stirred at -10° for 6 h to give 56% (S)-II (R = H). This was treated with HCl in toluene at 0° for 2 h to give 49% (S)-I (R = H) (92.1% e.e.).

IT

832745-40-1 1001921-20-5

RL: CAT (Catalyst use); USES (Uses)

(preparation of optically-active tert-Bu α-

(trifluoroethyl)phenylalaninates. and their intermediates)

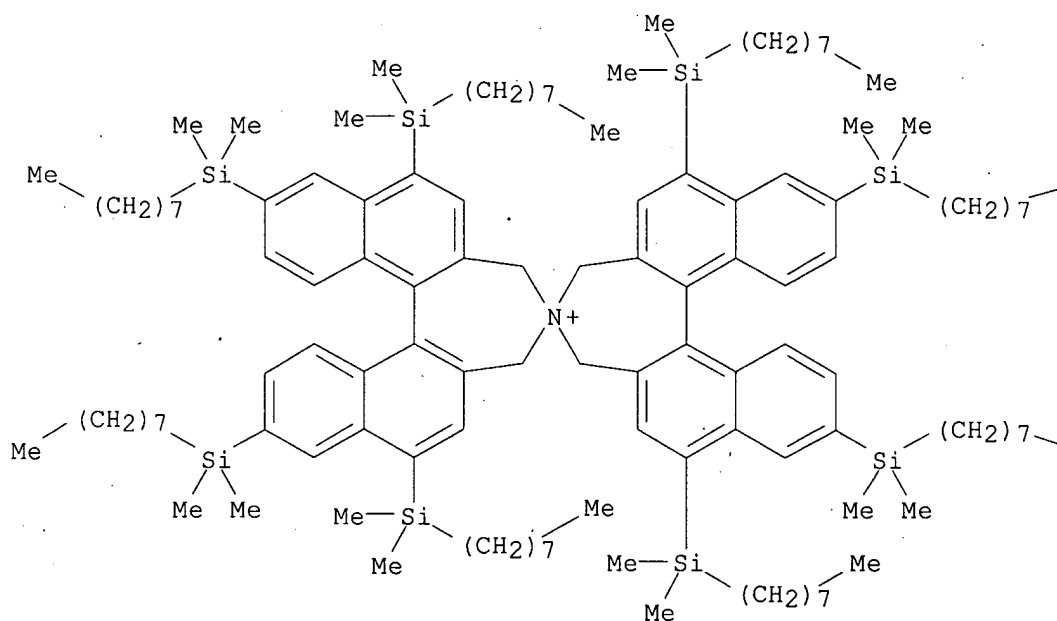
RN

832745-40-1 CAPLUS

CN

4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 1,1',7,7',9,9',14,14'-octakis(dimethyloctylsilyl)-3,3',5,5'-tetrahydro-, bromide (1:1), (11bR,11'bR)- (CA INDEX NAME)

PAGE 1-A



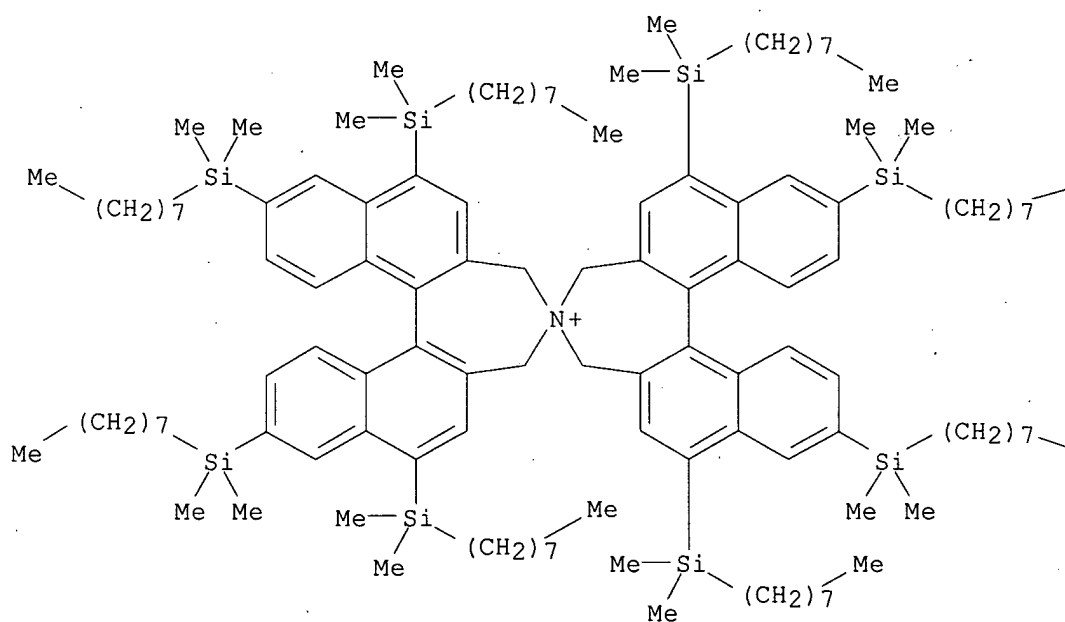
Me

● Br<sup>-</sup>

Me

RN 1001921-20-5 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 1,1',7,7',9,9',14,14'-  
 octakis(dimethyloctylsilyl)-3,3',5,5'-tetrahydro-, bromide (1:1),  
 (11bS,11'bS)- (CA INDEX NAME)

PAGE 1-A



Me

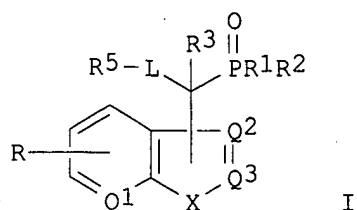
● Br<sup>-</sup>

Me

L3 ANSWER 3 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2007:1331354 CAPLUS  
 DOCUMENT NUMBER: 147:541994  
 TITLE: Phosphorus-containing benzothiophene and benzofuran  
 antagonists of transient cold receptor potential  
 channels (TRPM8) as antihyperalgesic and antiallodynic  
 agents for treatment of abnormal cold sensitivity and  
 pain  
 INVENTOR(S): Colburn, Raymond W.; Dax, Scott L.; Flores,  
 Christopher; Matthews, Jay; Qin, Ning; Youngman, Mark  
 A.; Teleha, Christopher; Reany, Laura  
 PATENT ASSIGNEE(S): Janssen Pharmaceutica N.V., Belg.  
 SOURCE: PCT Int. Appl., 423pp.  
 CODEN: PIXXD2  
 DOCUMENT TYPE: Patent  
 LANGUAGE: English  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2007134107	A2	20071122	WO 2007-US68566	20070509
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW			
RW:	AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG, BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM			
US 20080027029	A1	20080131	US 2007-746318	20070509
PRIORITY APPLN. INFO.:			US 2006-799275P	P 20060510
			US 2007-915527P	P 20070502

OTHER SOURCE(S): MARPAT 147:541994  
 GI



AB Phosphorylalkyl heterocyclic compds. I, preferably 2-phosphorylalkyl benzo[b]thiophenes, benzofurans and pyrido[2,3-b]thiophenes [1a; Q1 = CH, N; R = H, halo, C1-2 alkyl(oxy), OH, C1-2 alkoxy carbonyl, (alkyl)aminocarbonyl, CF<sub>3</sub>; X = O, S, SO, SO<sub>2</sub>; Q2 = CMe, CH, CPh, CBr, CCl, CCF<sub>3</sub>, imino; Q3 = C, CH, preferably Q3 = C; L = bond, alkylene, oxyalkylene, CH, preferably L = CH<sub>2</sub>, OCH<sub>2</sub>; R1, R2 = C1-8 alkyl(oxy), alkoxyalkyl, aryl, preferably R1, R2 = ethoxy, isopropoxy, butyl; R3 = H, Me; R5 = H, aryl, heteroaryl, preferably R5 = halophenyl, alkylphenyl, methoxyphenyl, 2-naphthyl, biphenyl, benzothienyl, benzo(1,3)dioxolyl, oxazolyl, thienyl, furyl, benzofuryl], useful as antiinflammatory and analgesic agents, cold menthol receptor (TRPM8) antagonists, were prepared by heterocyclization, Arbuzov phosphorylation and  $\alpha$ -alkylation of the phosphonates; the compds. were tested in vitro for TRPM8 receptor inhibition and in vivo for treatment of skin hypersensitivity and anxiety syndromes. In an example, di-Et 2-(4-fluorophenyl)-1-(3-methyl-2-benzo[b]thienyl)ethylphosphonate (50) was prepared by Arbuzov phosphorylation of 2-(bromomethyl)-3-methylbenzo[b]thiophene, followed by  $\alpha$ -benzylation of the di-Et (3-methyl-2-benzo[b]thienyl)phosphonate by BuLi/1,4-BrCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>F. In another example, the compound 50 at 1  $\mu$ M concentration exhibited in vitro 99% inhibition of canine TRPM8 ion channel activity induced by icilin. Pharmaceutical and veterinary compns. and methods of treating pain and various other disease states or conditions using compds. of the invention are also described.

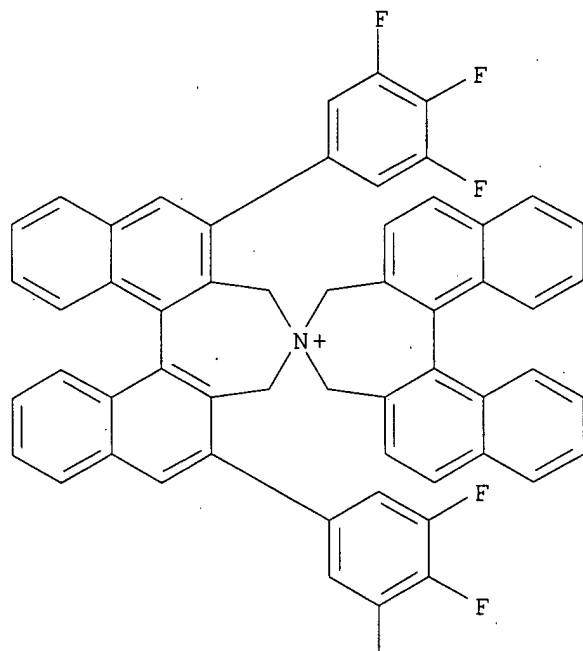
IT 287384-12-7 534570-50-8

RL: CAT (Catalyst use); USES (Uses)

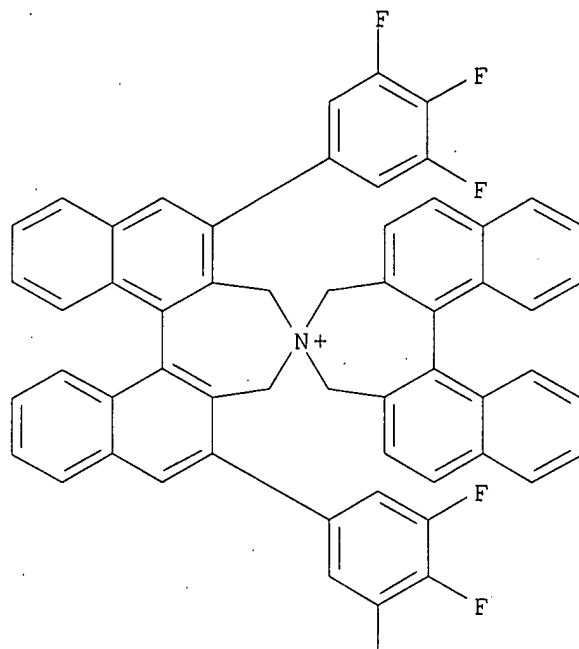
(preparation of  $\alpha$ -alkylated benzo[b]thienyl- and benzofurylalkyl phosphonates as cold menthol TRPM8 receptors antagonists for treatment of skin hypersensitivity and neuralgia disorders)

RN 287384-12-7 CAPLUS

CN 4,4'-Spiro[bi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



RN 534570-50-8 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
 2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bR,11'bR)- (CA INDEX  
 NAME)



L3 ANSWER 4 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2007:975541 CAPLUS  
 DOCUMENT NUMBER: 147:486636  
 TITLE: Practical Stereoselective Synthesis of  $\beta$ -Branched  
 $\alpha$ -Amino Acids through Efficient Kinetic  
 Resolution in the Phase-Transfer-Catalyzed Asymmetric  
 Alkylations  
 AUTHOR(S): Ooi, Takashi; Kato, Daisuke; Inamura, Koji; Ohmatsu,  
 Kohsuke; Maruoka, Keiji  
 CORPORATE SOURCE: Department of Chemistry, Graduate School of Science,  
 Kyoto University, Sakyo, Kyoto, 606-8502, Japan  
 SOURCE: Organic Letters (2007), 9(20), 3945-3948  
 CODEN: ORLEF7; ISSN: 1523-7060  
 PUBLISHER: American Chemical Society  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 OTHER SOURCE(S): CASREACT 147:486636  
 GI



AB Alkylation of glycinate Schiff base,  $\text{Ph}_2\text{C:NCH}_2\text{CO}_2\text{Bu-t}$ , with racemic secondary alkyl halides,  $\text{ArCH(Me)Br}$  ( $\text{Ar} = \text{Ph}, \text{C}_6\text{H}_4\text{F-4}, \text{C}_6\text{H}_4\text{Me-4}, 2\text{-naphthyl}, \text{C.tplbond.CPh}, \text{CO}_2\text{Bu-t}$ ), proceeded with excellent levels of syn- and anti- enantioselectivities under the influence of phase transfer catalyst, chiral quaternary ammonium bromide I, and 18-crown-6. In addition to the preparation of all the stereoisomers of  $\beta$ -alkyl- $\alpha$ -amino acid derivs., the syn alkylation product can be selectively converted to the corresponding anti isomer, a valuable chiral building block.

IT 287384-12-7 501934-20-9 501934-21-0

503538-60-1

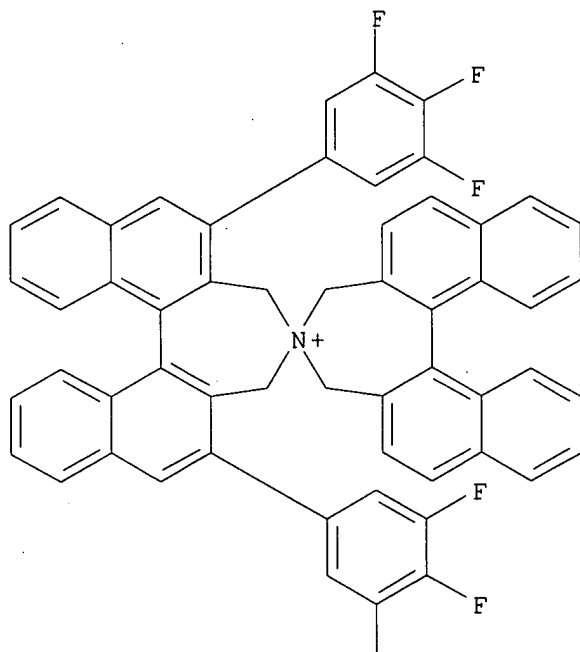
RL: CAT (Catalyst use); USES (Uses)

(preparation of branched amino acids via asym. alkylations of (diphenylmethylene)glycinate with alkyl bromides in presence of a chiral phase transfer catalyst)

RN 287384-12-7 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)

PAGE 1-A

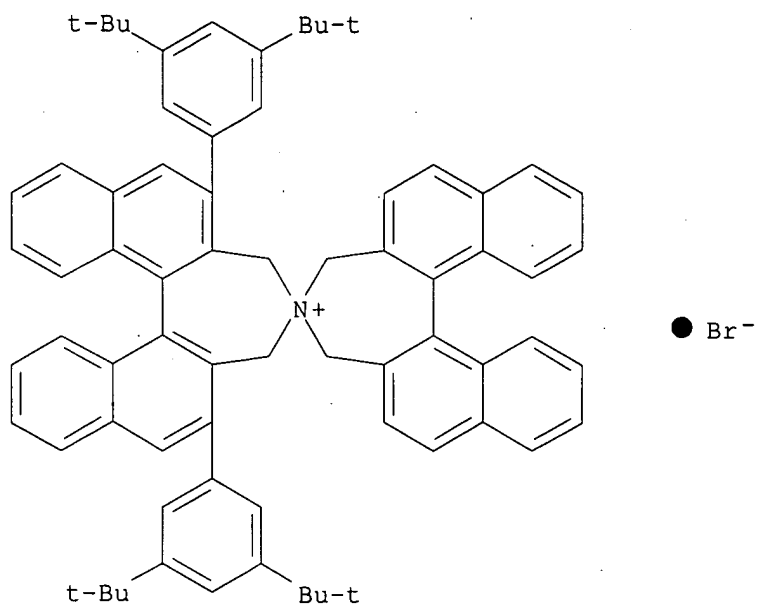


PAGE 2-A



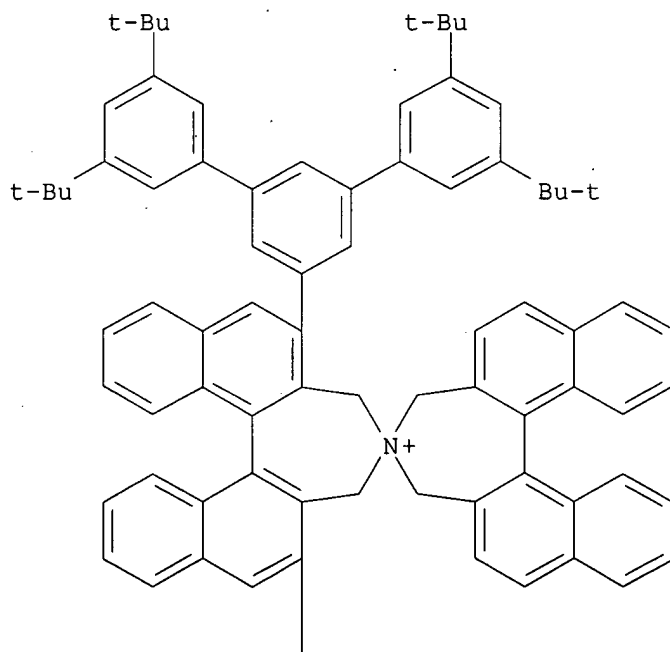
RN 501934-20-9 CAPLUS

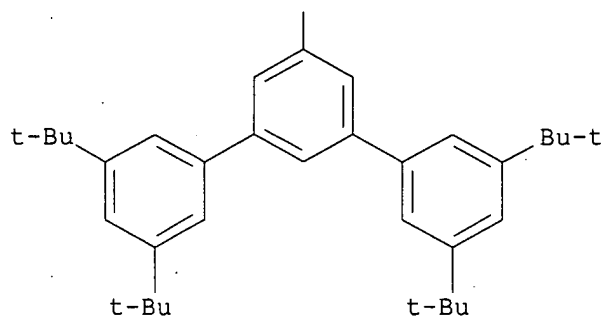
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(1,1-dimethylethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



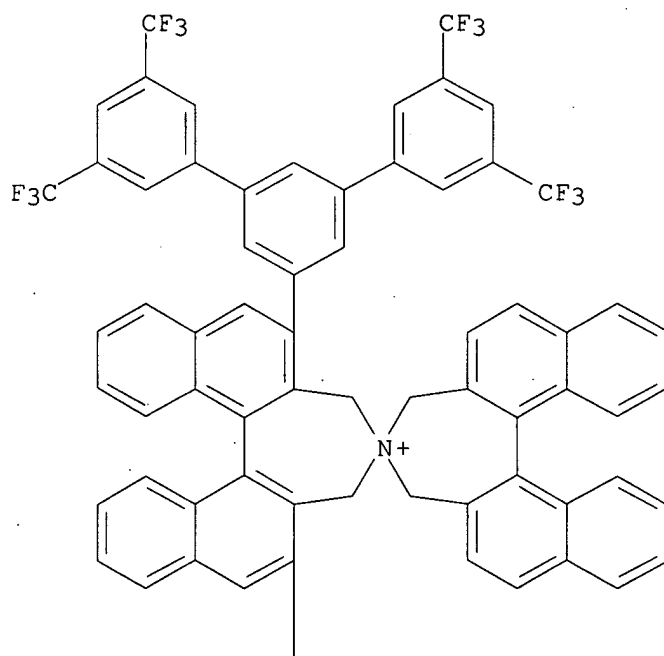
RN 501934-21-0 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[3,3'',5,5''-tetrakis(1,1-dimethylethyl)[1,1':3',1''-terphenyl]-5'-yl]-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)

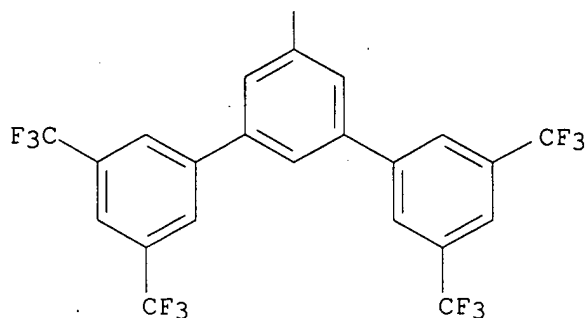
PAGE 1-A





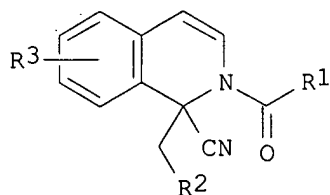
RN 503538-60-1 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
 2,6-bis[3,3'',5,5''-tetrakis(trifluoromethyl)[1,1':3',1''-terphenyl]-5'-  
 yl]-, bromide (1:1), (11bS,11'bs)- (CA INDEX NAME)





REFERENCE COUNT: 31 THERE ARE 31 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 5 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2007:965760 CAPLUS  
 DOCUMENT NUMBER: 147:469207  
 TITLE: Organocatalytic asymmetric destruction of 1-benzylated Reissert compounds catalysed by quaternary cinchona alkaloids  
 AUTHOR(S): Frisch, Kim; Jorgensen, Karl Anker  
 CORPORATE SOURCE: Danish National Research Foundation: Center for Catalysis, Department of Chemistry, Aarhus University, Aarhus, DK-8000, Den.  
 SOURCE: Organic & Biomolecular Chemistry (2007), 5(18), 2966-2974  
 CODEN: OBCRAK; ISSN: 1477-0520  
 PUBLISHER: Royal Society of Chemistry  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 OTHER SOURCE(S): CASREACT 147:469207  
 GI

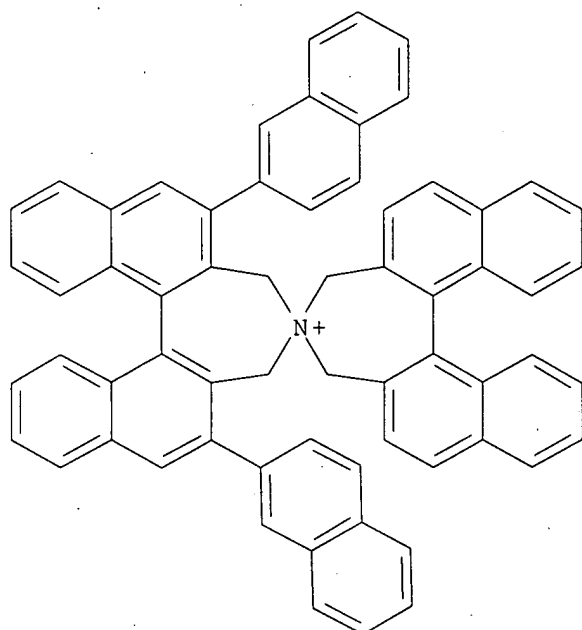


I

AB The enantiomeric enrichment of racemic 1-benzylated Reissert compds. I [R1 = Me, Me2CH, Ph, 4-MeOC6H4, 4-BrC6H4, 3,5-(MeO)2C6H3; R2 = Ph, 4-MeOC6H4, 4-NCC6H4; R3 = H, 4-Br, 5-Br, 5-MeO] under organocatalytic biphasic conditions is presented. The enrichment is the consequence of an asym. destruction of the racemic compds. I resulting in the formation of the corresponding 1-benzylated isoquinolines. The highest selectivity has been achieved using quaternary cinchona alkaloids as phase-transfer catalysts. The resolution of a number of racemic 1-benzylated Reissert compds. reveals a significant substrate dependence and a proposal for the mechanism of the reaction is presented.

IT 237762-42-4  
 RL: CAT (Catalyst use); USES (Uses)  
 (asym. destruction/kinetic resolution of 1-benzylated Reissert compds.)

catalyzed by quaternary cinchona alkaloids)  
 RN 237762-42-4 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
 2,6-di-2-naphthalenyl-, bromide (1:1), (11bS,11'bs)- (CA INDEX NAME)



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REFERENCE COUNT: 83 THERE ARE 83 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 6 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2007:728784 CAPLUS  
 DOCUMENT NUMBER: 147:142788  
 TITLE: Catalyst capable of allowing Strecker reaction to proceed stereoselectively and method for stereoselectively producing  $\alpha$ -aminonitrile derivative using the same  
 INVENTOR(S): Maruoka, Keiji; Ooi, Takashi  
 PATENT ASSIGNEE(S): Nagase & Co., Ltd., Japan; Kyoto University  
 SOURCE: PCT Int. Appl., 396pp.  
 CODEN: PIXXD2  
 DOCUMENT TYPE: Patent  
 LANGUAGE: Japanese  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2007074553	A1	20070705	WO 2006-JP314023	20060707
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW			
RW:	AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG, BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM			

PRIORITY APPLN. INFO.:

JP 2005-373490

A 20051226

AB According to the invention, a catalyst for a Strecker reaction comprising a quaternary ammonium salt and a method for stereoselectively producing an  $\alpha$ -aminonitrile derivative using the same are provided. By using the  $\alpha$ -aminonitrile derivative obtained by the invention, an optically active  $\alpha$ -amino acid and a derivative thereof, which were difficult to produce by a conventional alkylation reaction can be easily produced.

IT 466679-93-6 534570-50-8

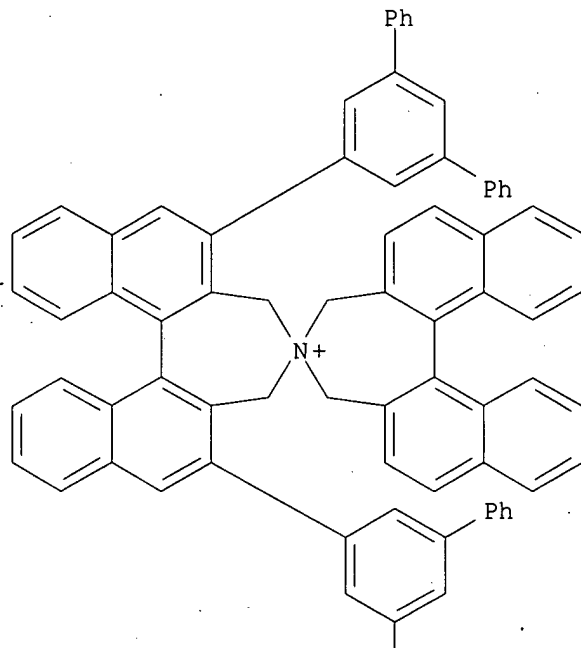
RL: CAT (Catalyst use); TEM (Technical or engineered material use); USES (Uses)

(catalyst capable of allowing Strecker reaction to proceed stereoselectively and method for stereoselectively producing  $\alpha$ -aminonitrile derivative using the same)

RN 466679-93-6 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis([1,1':3',1''-terphenyl]-5'-yl)-3,3',5,5'-tetrahydro-, bromide (1:1), (11bR,11'bR)- (CA INDEX NAME)

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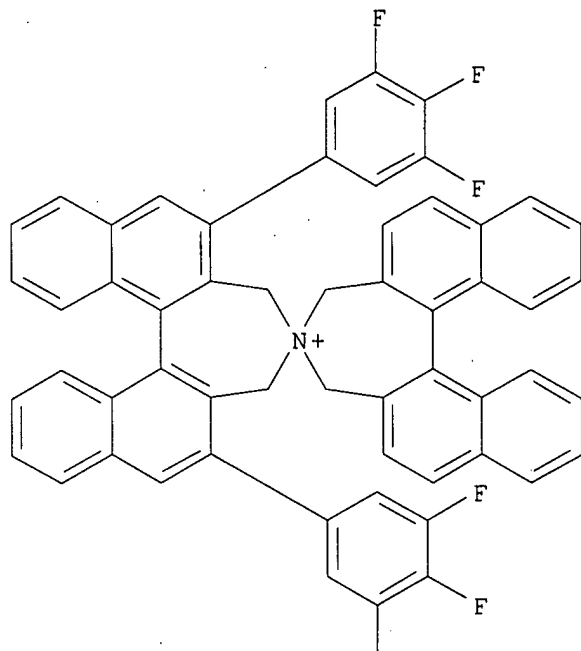


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RN 534570-50-8 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bR,11'bR)- (CA INDEX NAME)



REFERENCE COUNT: 20 THERE ARE 20 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 7 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2007:617770 CAPLUS

DOCUMENT NUMBER: 147:212249

TITLE: Solvent effects in the enantioselective catalytic-phase-transfer alkylation of polymer-supported glycine-imine tert-butyl ester: asymmetric solid-phase synthesis of (R)- $\alpha$ -amino acid derivatives

AUTHOR(S): Kim, Mi-Jeong; Jew, Sang-sup; Park, Hyeung-geun; Jeong, Byeong-Seon

CORPORATE SOURCE: Research Institute of Pharmaceutical Science and College of Pharmacy, Seoul National University, Seoul, 151-742, S. Korea

SOURCE: European Journal of Organic Chemistry (2007), (15), 2490-2496

CODEN: EJOCFK; ISSN: 1434-193X

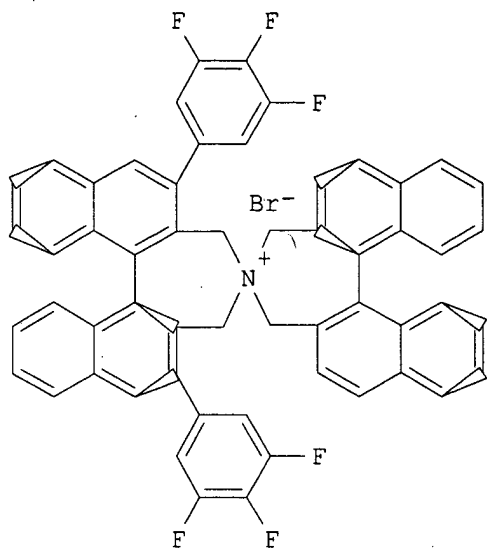
PUBLISHER: Wiley-VCH Verlag GmbH & Co. KGaA

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 147:212249

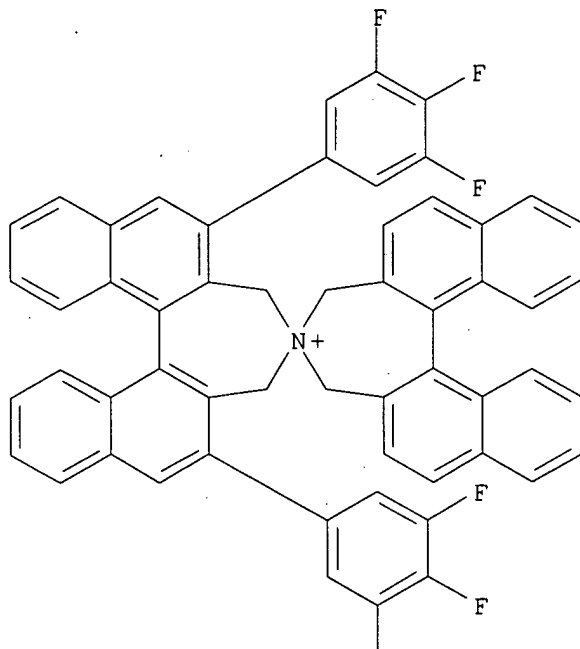
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- AB Polymer-supported glycine Schiff base tert-Bu esters (Resin-CH:NCH<sub>2</sub>CO<sub>2</sub>Bu-t; Resin = Merrifield, Wang) were prepared from Merrifield or Wang resins, and were used in the enantioselective synthesis of (R)- $\alpha$ -amino acids by using (S,S)-3,4,5-trifluorophenyl-NAS bromide (I) as the chiral phase-transfer catalyst. The chemical yields and enantioselectivities were found to be dramatically dependent upon the ratio of water to organic solvent. The optimal solvent was a mixture of toluene/chloroform/water (9:1:0.5). The enantioselective solid-phase phase-transfer catalytic alkylation of Merrifield resin-supported glycine Schiff base tert-Bu ester with various alkyl bromides in presence of 50% aqueous CsOH in the optimal solvent system at 0° followed by hydrolysis and benzoylation afforded the corresponding (R)-N-benzoylamino acid tert-Bu esters in 60-80% yields with enantiomeric ratios of 96.5:3.5 to 99.5:0.5.
- IT 287384-12-7  
 RL: CAT (Catalyst use); USES (Uses)  
 (solvent effects in asym. alkylation of polymer-supported glycinate Schiff base with alkyl bromides in presence of phase transfer catalysts)
- RN 287384-12-7 CAPLUS
- CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)





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REFERENCE COUNT: 24 THERE ARE 24 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 8 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2007:401075 CAPLUS

DOCUMENT NUMBER: 148:168560

TITLE: Effects of aromatic substituents on binaphthyl-based chiral spiro-type ammonium salts in asymmetric phase-transfer reactions

AUTHOR(S): Kano, Taichi; Lan, Quan; Wang, Xisheng; Maruoka, Keiji

CORPORATE SOURCE: Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo, Kyoto, 606-8502, Japan

SOURCE: Advanced Synthesis & Catalysis (2007), 349(4+5), 556-560

CODEN: ASCAF7; ISSN: 1615-4150

PUBLISHER: Wiley-VCH Verlag GmbH & Co. KGaA

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 148:168560

AB Spiro-type phase-transfer catalysts prepared from two equivalent of a single binaphthyl subunit were designed and applied to the asym. alkylation and direct aldol reactions of glycine derivative Ph<sub>2</sub>C:NCH<sub>2</sub>CO<sub>2</sub>CMe<sub>3</sub>. The effects of the substitution pattern of the binaphthyl subunits on the enantioselectivity were also investigated.

IT 1002330-65-5P

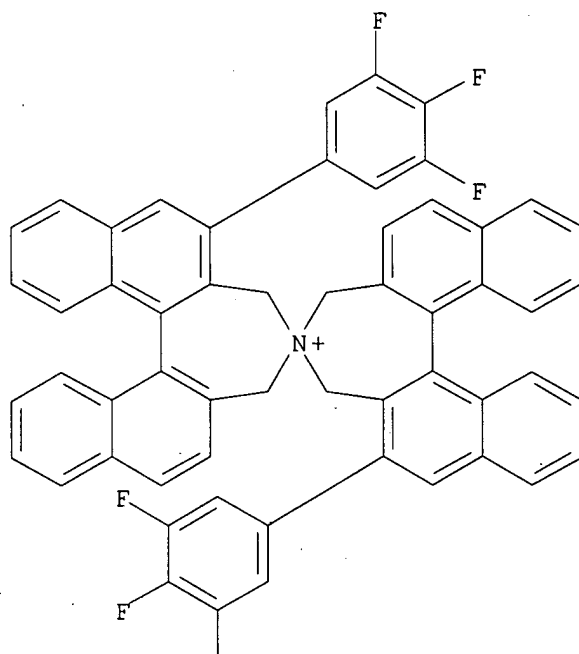
RL: CAT (Catalyst use); PRP (Properties); SPN (Synthetic preparation);  
PREP (Preparation); USES (Uses)

(crystal structure; effects of aromatic substituents on binaphthyl-based  
chiral spiro-type ammonium salts in asym. phase-transfer alkylation and  
direct aldol condensation reactions)

RN 1002330-65-5 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
2,2'-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bS)- (CA INDEX  
NAME)

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IT 1002330-75-7P

RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)  
(crystal structure; effects of aromatic substituents on binaphthyl-based  
chiral spiro-type ammonium salts in asym. phase-transfer alkylation and  
direct aldol condensation reactions)

RN 1002330-75-7 CAPLUS

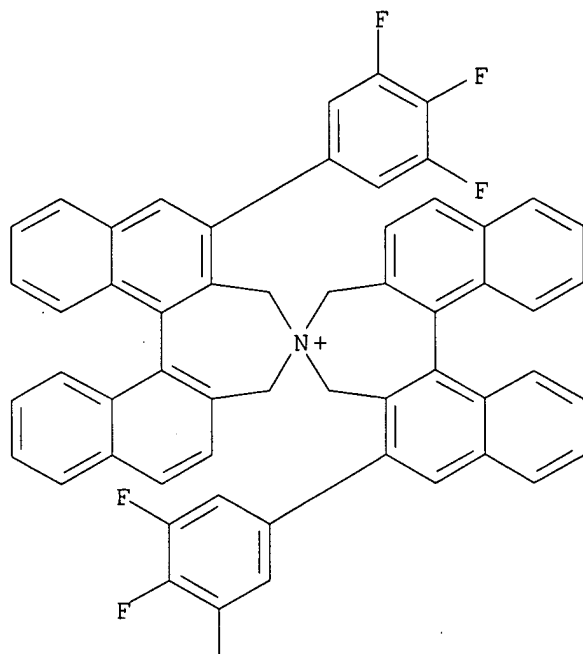
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
2,2'-bis(3,4,5-trifluorophenyl)-, bromide, (11bS,11'bS)-, compd. with  
dichloromethane (1:1:1) (CA INDEX NAME)

CM 1

CRN 1002330-65-5

CMF C56 H34 F6 N . Br

PAGE 1-A



PAGE 2-A

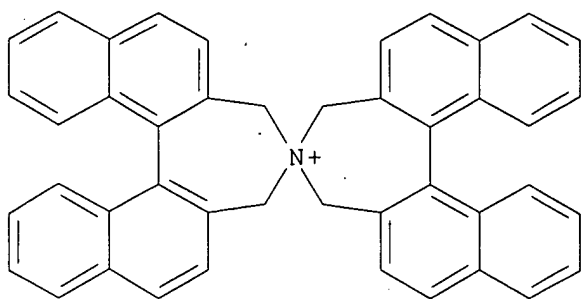


CM 2

CRN 75-09-2  
CMF C H2 Cl2

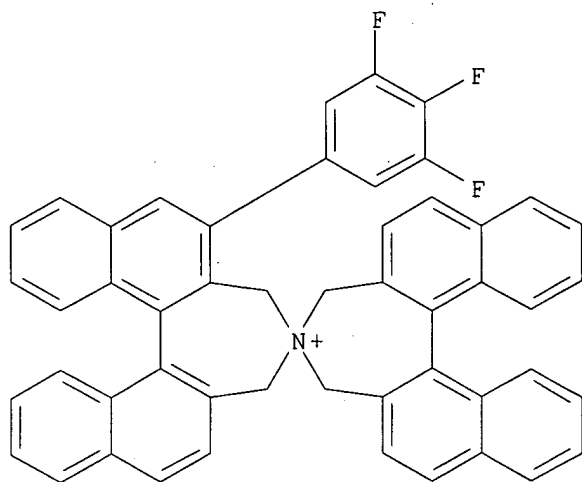
Cl-CH<sub>2</sub>-Cl

IT 237762-40-2 1002330-66-6  
RL: CAT (Catalyst use); USES (Uses)  
(effects of aromatic substituents on binaphthyl-based chiral spiro-type  
ammonium salts in asym. phase-transfer alkylation and direct aldol  
condensation reactions)  
RN 237762-40-2 CAPLUS  
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-,  
bromide (1:1), (11bS,11'bs)- (CA INDEX NAME)



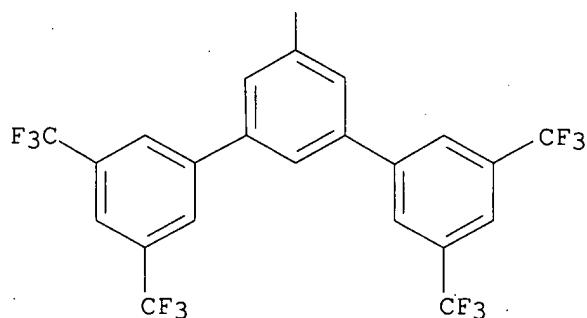
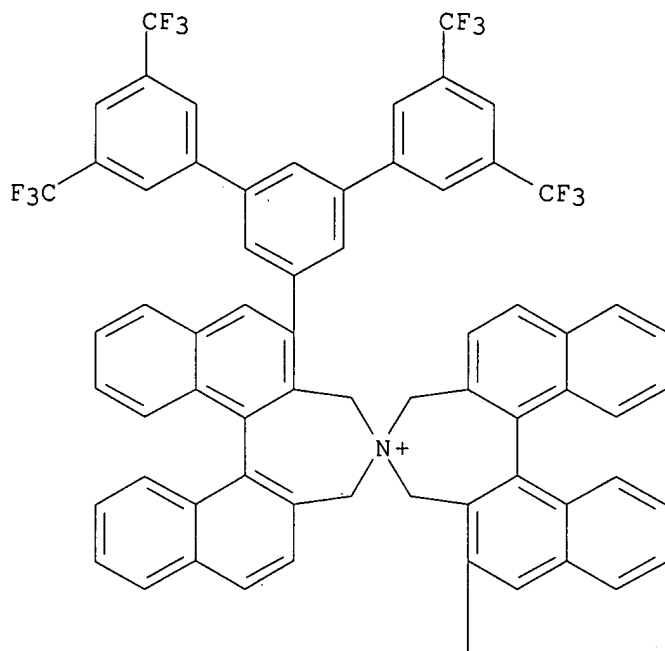
● Br<sup>-</sup>

RN 1002330-66-6 CAPLUS  
 CN 4,4'-Spiro[4H-dinaphth[2,1-c:1',2'-e]azepin-2-ylidene]-3,3',5,5'-tetrahydro-2-(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



● Br<sup>-</sup>

IT 1002330-67-7P  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
 USES (Uses)  
 (effects of aromatic substituents on binaphthyl-based chiral spiro-type  
 ammonium salts in asym. phase-transfer alkylation and direct aldol  
 condensation reactions)  
 RN 1002330-67-7 CAPLUS  
 CN 4,4'-Spiro[4H-dinaphth[2,1-c:1',2'-e]azepin-2-ylidene]-3,3',5,5'-tetrahydro-2,2'-bis[3,3',5,5'-tetrakis(trifluoromethyl)[1,1':3',1''-terphenyl]-5'-yl]-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



REFERENCE COUNT: 36 THERE ARE 36 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 9 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2007:366113 CAPLUS

DOCUMENT NUMBER: 146:521640

TITLE: Catalytic asymmetric alkylation of  $\alpha$ -cyano carboxylates using a phase-transfer catalyst

AUTHOR(S): Nagata, Kazuhiro; Sano, Daisuke; Itoh, Takashi

CORPORATE SOURCE: School of Pharmaceutical Sciences, Showa University, 1-5-8 Hatanodai, Shinagawa-ku, Tokyo, 142-8555, Japan

SOURCE: Synlett (2007), (4), 547-550  
CODEN: SYNLES; ISSN: 0936-5214

PUBLISHER: Georg Thieme Verlag

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 146:521640

AB The highly enantioselective catalytic alkylation of cyanoacetates was achieved using a chiral phase-transfer catalyst to give  $\alpha,\alpha$ -disubstituted  $\alpha$ -cyanoacetates which have a chiral quaternary carbon. The product thus obtained was applied to the synthesis of an optically active oxindole.

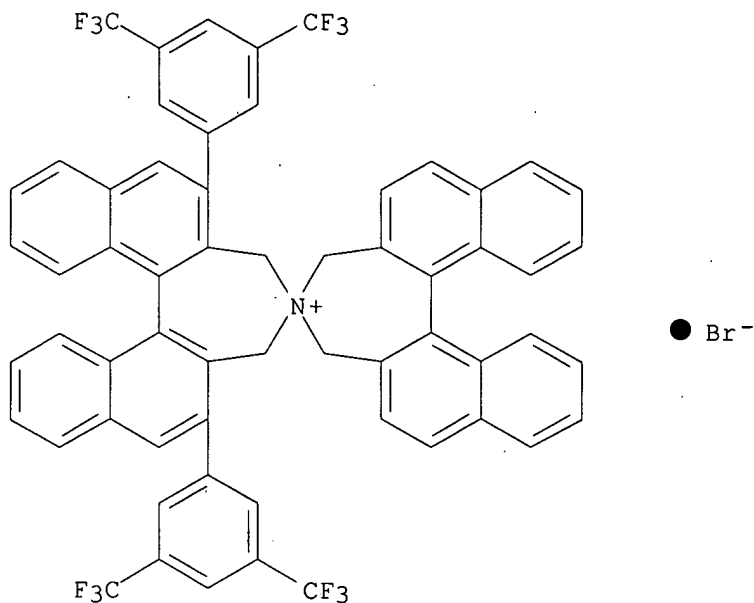
IT 515137-97-0 534570-50-8

RL: CAT (Catalyst use); USES (Uses)

(asym. alkylation of  $\alpha$ -cyanoacetates using phase-transfer catalyst)

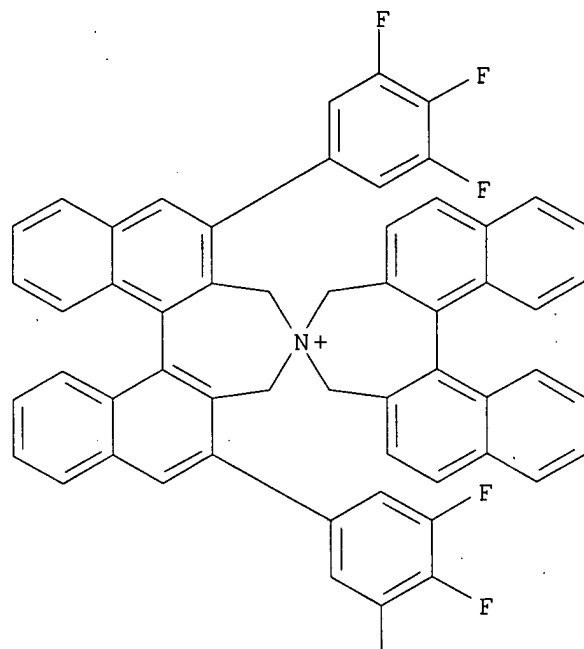
RN 515137-97-0 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide (1:1), (11bR,11'bR)- (CA INDEX NAME)



RN 534570-50-8 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bR,11'bR)- (CA INDEX NAME)



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● Br<sup>-</sup>

REFERENCE COUNT: 30 THERE ARE 30 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 10 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2007:114256 CAPLUS  
 DOCUMENT NUMBER: 146:206634  
 TITLE: Process for production of mono-substituted alkylated compound using aldimine or derivative thereof  
 INVENTOR(S): Maruoka, Keiji; Inoue, Toru; Matsumoto, Jun  
 PATENT ASSIGNEE(S): Nagase & Co., Ltd., Japan  
 SOURCE: PCT Int. Appl., 173pp.  
 CODEN: PIXXD2  
 DOCUMENT TYPE: Patent  
 LANGUAGE: Japanese  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2007013698	A1	20070201	WO 2006-JP315457	20060728
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HN, HR, HU, ID, IL, IN, IS, JP, KE, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU,				

SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG,  
 US, UZ, VC, VN, ZA, ZM, ZW  
 RW: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE,  
 IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ,  
 CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG, BW, GH,  
 GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY,  
 KG, KZ, MD, RU, TJ, TM

CA 2610776 A1 20070201 CA 2006-2610776 20060728  
 PRIORITY APPLN. INFO.: JP 2005-220757 A 20050729  
 JP 2005-348518 A 20051201  
 WO 2006-JP315457 W 20060728

OTHER SOURCE(S): MARPAT 146:206634

AB Disclosed is a process for producing an asym. mono-substituted alkylated compound of an  $\alpha$ -amino acid which is represented by a specific formula by using an aldimine-type Schiff base  $R15-[CH=N-CH(R18)COR20]_n$  [R15, R18 = independently (halo)alkyl, (halo)alkoxy, (halo)aryl, etc.; R20 = aryloxy, amino, alkyl, etc.; n = 1-4]. In the process, the alkylation of an aldimine-type Schiff base in a medium in the presence of an optically active quaternary ammonium salt phase transfer catalyst and an inorg. base is started, and subsequently the reaction is quenched at any time preceding the completion of the stoichiometrical reaction, thereby yielding a mono-substituted alkylated product having a high optical purity.

IT 503538-60-1 534570-50-8

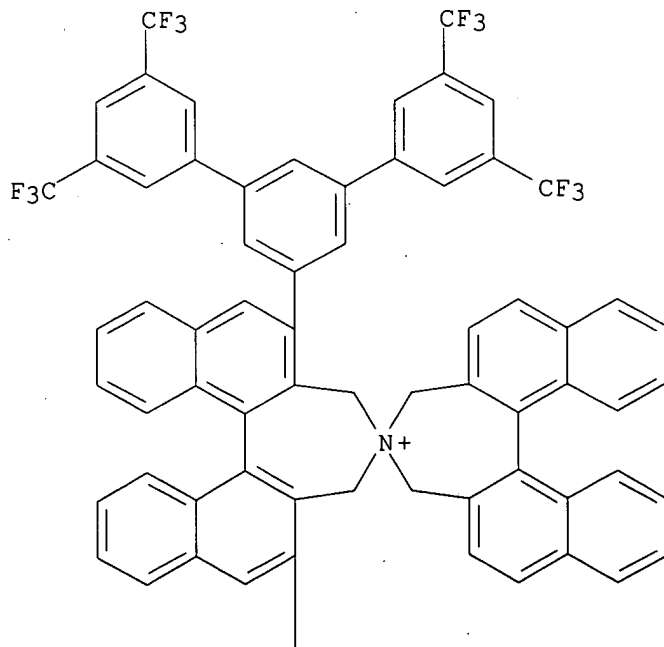
RL: CAT (Catalyst use); USES (Uses)

(preparation of mono-substituted alkylated compound using aldimine or derivative thereof)

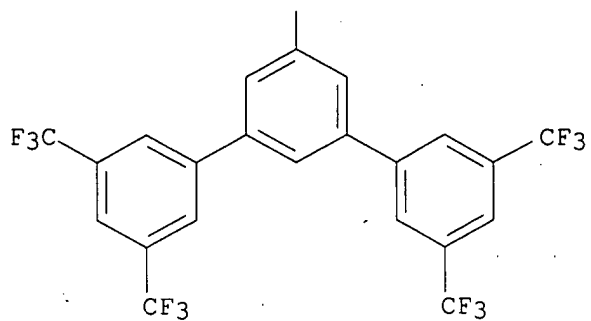
RN 503538-60-1 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[3,3'',5,5''-tetrakis(trifluoromethyl)[1,1':3',1''-terphenyl]-5'-yl]-, bromide (1:1), (11bS,11'bs)- (CA INDEX NAME)

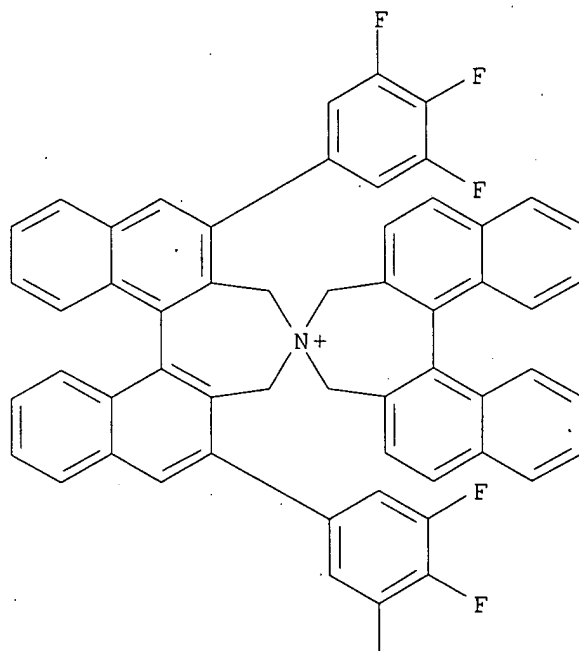
PAGE 1-A







RN 534570-50-8 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
 2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bR,11'bR)- (CA INDEX  
 NAME)



L3 ANSWER 11 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2006:1291889 CAPLUS

DOCUMENT NUMBER: 146:184133

TITLE: Highly diastereo- and enantioselective formal conjugate addition of nitroalkanes to nitroalkenes by chiral ammonium bifluoride catalysis

AUTHOR(S): Ooi, Takashi; Takada, Saki; Doda, Kanae; Maruoka, Keiji

CORPORATE SOURCE: Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo, Kyoto, 606-8502, Japan

SOURCE: Angewandte Chemie, International Edition (2006), 45(45), 7606-7608

CODEN: ACIEF5; ISSN: 1433-7851

PUBLISHER: Wiley-VCH Verlag GmbH & Co. KGaA

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 146:184133

AB A chiral quaternary ammonium bifluoride catalyst has been successfully used for highly diastereo- and enantioselective addition of silyl nitronates  $R_1CH:N^+(O^-)OSiMe_3$  ( $R_1 = Et, n-Pr, MeOCH_2$ ) to nitroalkenes  $R_2CH:CHNO_2$  ( $R_2 = n\text{-hexyl, cyclohexyl, Ph, 4-MeOC}_6\text{H}_4, 2\text{-furyl, etc.}$ ) which represents formal conjugate addition of nitroalkanes to nitroalkenes. The resulting 1,3-dinitro compds.  $R_1CH(NO_2)CH(R_2)CH_2NO_2$  bear two defined stereocenters, which can serve as versatile chiral building blocks in organic synthesis.

IT 586344-86-7 586344-89-0 586344-91-4

RL: CAT (Catalyst use); USES (Uses)

(asym. synthesis of 1,3-dinitro compds. via chiral ammonium bifluoride-catalyzed diastereo- and enantioselective conjugate addition of silyl nitronates to nitroalkenes)

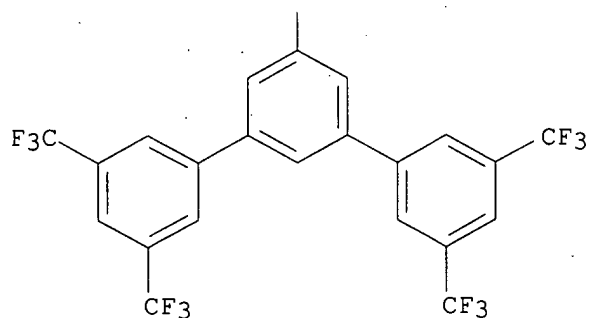
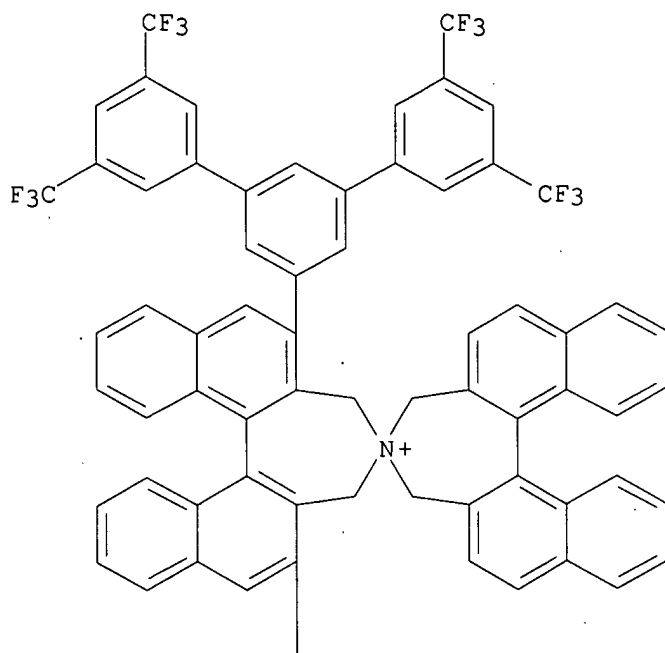
RN 586344-86-7 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[3,3'',5,5''-tetrakis(trifluoromethyl)[1,1':3',1''-terphenyl]-5'-yl]-, (11bR,11'bR)-, (hydrogen difluoride) (1:1) (CA INDEX NAME)

CM 1

CRN 586344-85-6

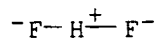
CMF C88 H48 F24 N



CM 2

CRN 18130-74-0

CMF F2 H



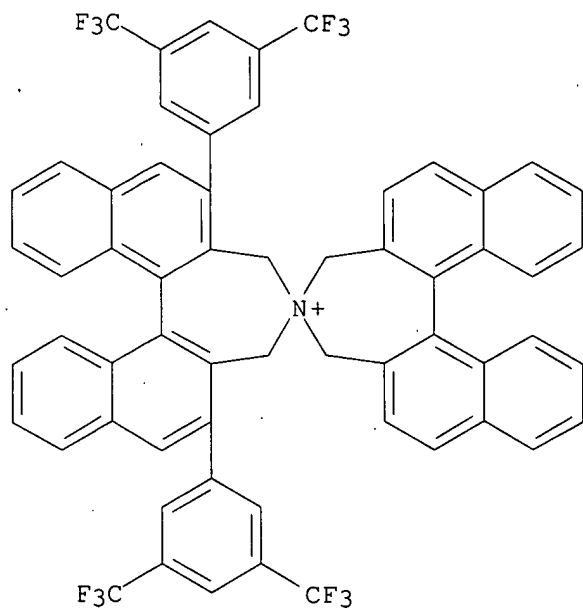
RN 586344-89-0 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, (11bR,11'bR)-, (hydrogen difluoride) (1:1) (CA INDEX NAME)

CM 1

CRN 586344-88-9

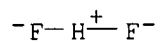
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CM 2

CRN 18130-74-0

CMF F2 H



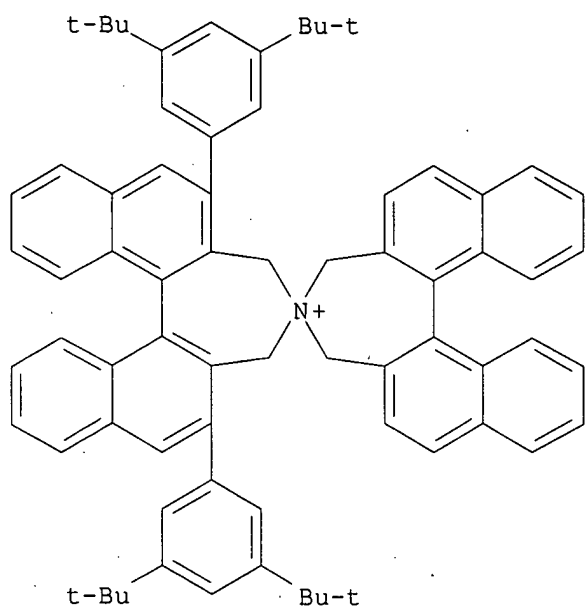
RN 586344-91-4 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(1,1-dimethylethyl)phenyl]-3,3',5,5'-tetrahydro-, (11bR,11'bR)-, (hydrogen difluoride) (1:1) (CA INDEX NAME)

CM 1

CRN 586344-90-3

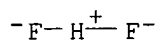
CMF C72 H72 N



CM 2

CRN 18130-74-0

CMF F2 H



REFERENCE COUNT: 24 THERE ARE 24 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 12 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2006:1133933 CAPLUS

DOCUMENT NUMBER: 146:45051

TITLE: Asymmetric phase-transfer catalysis of homo- and heterochiral quaternary ammonium salts: development and application of conformationally flexible chiral phase-transfer catalysts

AUTHOR(S): Ooi, Takashi; Uematsu, Yukitaka; Kameda, Minoru; Maruoka, Keiji

CORPORATE SOURCE: Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo, Kyoto, 606-8502, Japan

SOURCE: Tetrahedron (2006), 62(49), 11425-11436

CODEN: TETRAB; ISSN: 0040-4020

PUBLISHER: Elsevier Ltd.

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 146:45051

GI

\* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT \*

AB Inspired by the considerable difference of catalytic activity and stereocontrolling ability between the conformationally rigid, homo- and heterochiral quaternary ammonium bromides 1 (I), conformationally

flexible, N-spiro chiral quaternary ammonium bromides of type 4 (II) have been designed and synthesized. Reliable procedures for the preparation of the appropriately substituted biphenyl subunits have been established by the repeated use of ortho magnesiation-halogenation as a key synthetic tool. The relationship between the structure of achiral biphenyl moiety and the reactivity and selectivity of 4 has been evaluated in the asym. alkylation of glycinate Schiff base 2 (III) under typical phase-transfer conditions, leading to the identification of 4l (Arl = 3,5,-Ph<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>) as an optimal catalyst structure to exhibit an excellent enantiocontrol in the reactions with various alkyl halides. The mol. structure of 4l was determined by X-ray crystallog. anal. and its unique behavior in solution was examined by a variable-temperature <sup>1</sup>H NMR study. These investigations uncovered that the observed high chiral efficiency originated from the efficient asym. phase-transfer catalysis of homochiral-4l, which rapidly equilibrated with heterochiral-4l of low catalytic activity and stereoselectivity.

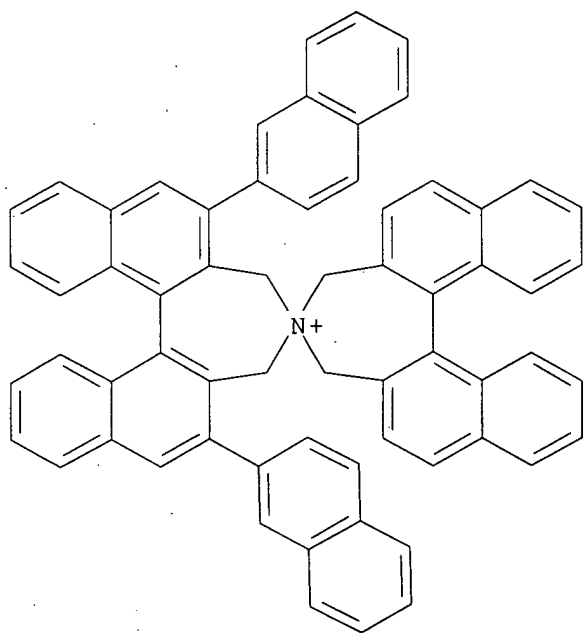
IT 452067-26-4

RL: CAT (Catalyst use); USES (Uses)

(reduction; esterification; asym. phase-transfer catalysis of homo- and heterochiral quaternary ammonium salts, development and application of conformationally flexible chiral phase-transfer catalysts)

RN 452067-26-4 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-di-2-naphthalenyl-, bromide, (11bR,11'bS)- (CA INDEX NAME)



● Br<sup>-</sup>

REFERENCE COUNT: 55 THERE ARE 55 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT.

L3 ANSWER 13 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2006:898487 CAPLUS

DOCUMENT NUMBER: 146:441599

TITLE: Asymmetric synthesis of  $\alpha$ -acyl- $\gamma$ -butyrolactones possessing all-carbon quaternary stereocenters by phase-transfer-catalyzed alkylation  
AUTHOR(S): Ooi, Takashi; Miki, Takashi; Fukumoto, Kazuhiro; Maruoka, Keiji

CORPORATE SOURCE: Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo, Kyoto, 606-8502, Japan

SOURCE: Advanced Synthesis & Catalysis (2006), 348(12+13), 1539-1542

CODEN: ASCAF7; ISSN: 1615-4150

PUBLISHER: Wiley-VCH Verlag GmbH & Co. KGaA

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 146:441599

AB The enantioselective construction of all-C quaternary stereocenters on  $\alpha$ -acyl- $\gamma$ -butyrolactones was achieved by the N-spiro chiral quaternary ammonium bromide 1-catalyzed alkylation under mild phase-transfer conditions. For example, 91 % (91 %ee) (3S)-3-benzoyl-3-benzyltetrahydrofuran-2-one was obtained from BnBr and 3-benzoyltetrahydrofuran-2-one using Cs<sub>2</sub>CO<sub>3</sub> in toluene at -20°. The resulting  $\alpha$ -alkylated keto lactones serve as valuable chiral building blocks in organic synthesis as clearly demonstrated by the facile conversion to optically active  $\alpha,\alpha$ -dialkyl- $\alpha$ -amino acid derivs. via Schmidt rearrangement.

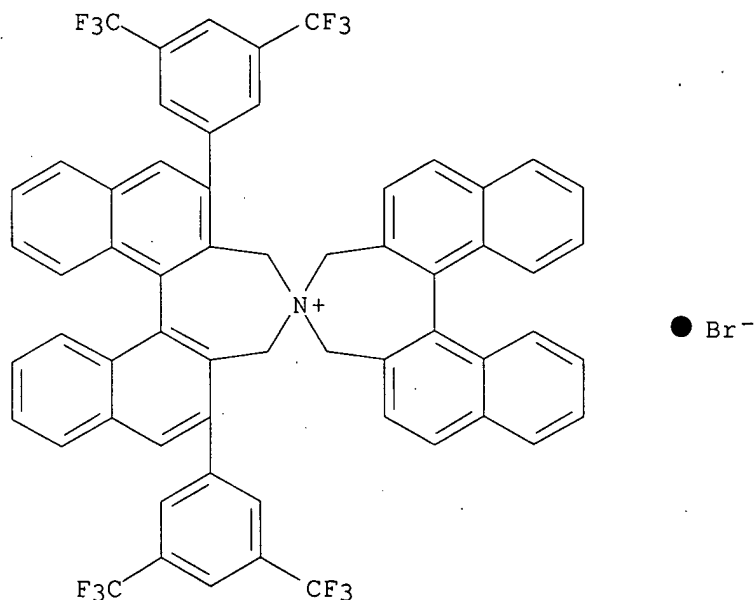
IT 438002-03-0

RL: CAT (Catalyst use); USES (Uses)

(best catalyst; asym. synthesis of  $\alpha$ -acyl- $\gamma$ -butyrolactones possessing all-carbon quaternary stereocenters by phase-transfer-catalyzed alkylation)

RN 438002-03-0 CAPLUS

CN 8,8'-Spirobi[8H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



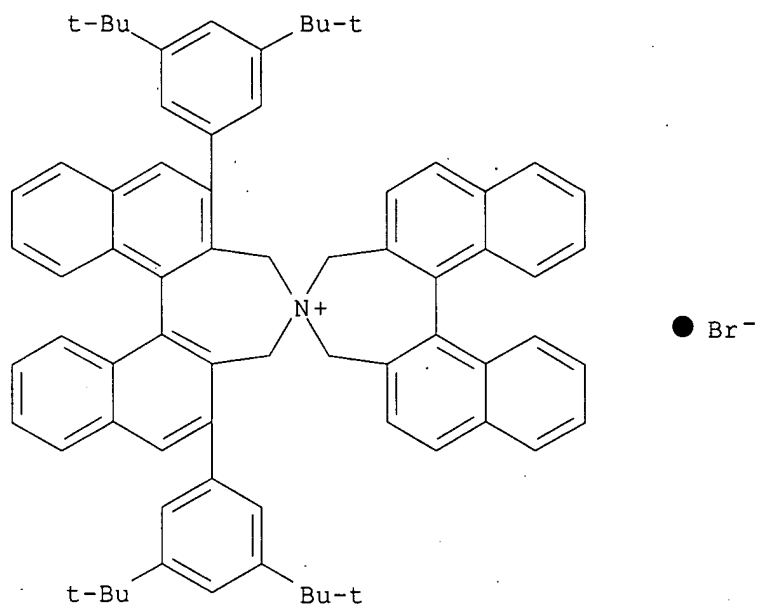
IT 501934-20-9 503538-60-1

RL: CAT (Catalyst use); USES (Uses)

(catalyst comparison; asym. synthesis of  $\alpha$ -acyl- $\gamma$ -butyrolactones possessing all-carbon quaternary stereocenters by phase-transfer-catalyzed alkylation)

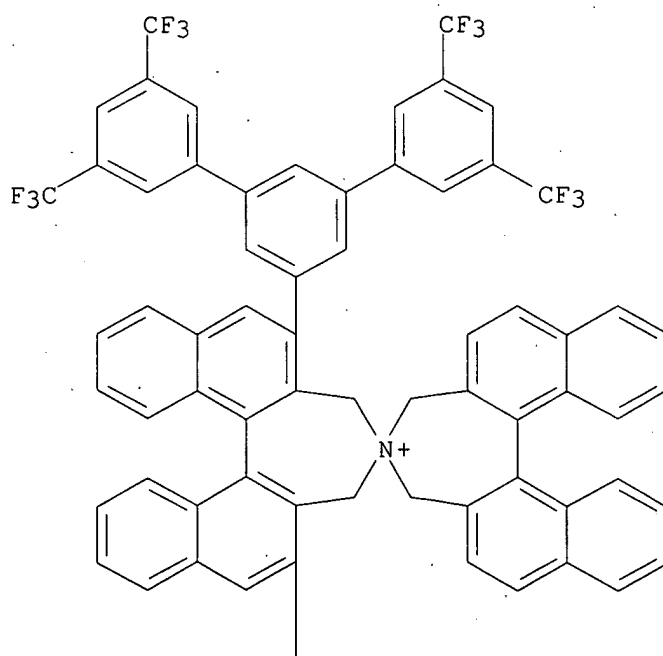
RN 501934-20-9 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(1,1-dimethylethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)

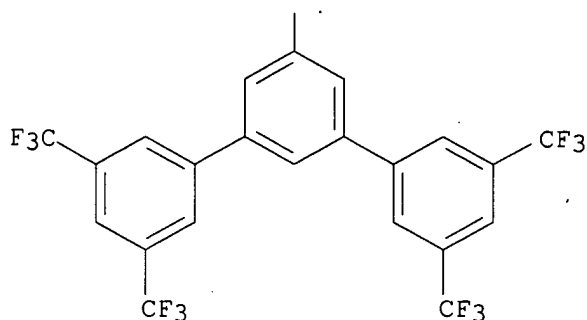


RN 503538-60-1 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
 2,6-bis[3,3'',5,5''-tetrakis(trifluoromethyl)[1,1':3',1''-terphenyl]-5'-  
 yl]-, bromide (1:1), (11bS,11'bs)- (CA INDEX NAME)

PAGE 1-A







● Br<sup>-</sup>

REFERENCE COUNT: 32 THERE ARE 32 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 14 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2006:594632 CAPLUS

DOCUMENT NUMBER: 145:230377

TITLE: Construction of enantiomerically enriched tertiary  $\alpha$ -hydroxycarboxylic acid derivatives by phase-transfer-catalyzed asymmetric alkylation of diaryloxazolidine-2,4-diones

AUTHOR(S): Ooi, Takashi; Fukumoto, Kazuhiro; Maruoka, Keiji  
CORPORATE SOURCE: Department of Chemistry Graduate School of Science, Kyoto University, Sakyo, Kyoto, 606-8502, Japan

SOURCE: Angewandte Chemie, International Edition (2006), 45(23), 3839-3842

CODEN: ACIEF5; ISSN: 1433-7851

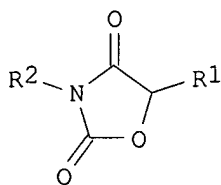
PUBLISHER: Wiley-VCH Verlag GmbH & Co. KGaA

DOCUMENT TYPE: Journal

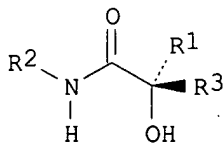
LANGUAGE: English

OTHER SOURCE(S): CASREACT 145:230377

GI



I



II

AB The chiral binaphthalene-based ammonium bromide has been used as a catalyst for the highly enantioselective alkylation of 3,5-diaryl 2,4-oxazolidinediones I (R1 = Ph, 4-FC6H4, 4-MeOC6H4, 2-furyl, 2-thienyl, R2 = Ph; R1 = Ph, R2 = 4-FC6H4, 4-MeOC6H4) under mild phase-transfer conditions. This method provides practical access to a variety of optically active tertiary  $\alpha$ -hydroxycarboxylic acid amides II (R3 = HC.tplbond.CCH2, H2C:CHCH2, H2C:CMeCH2, PhCH2, 4-MeC6H4CH2, 1-naphthylmethyl, etc.).

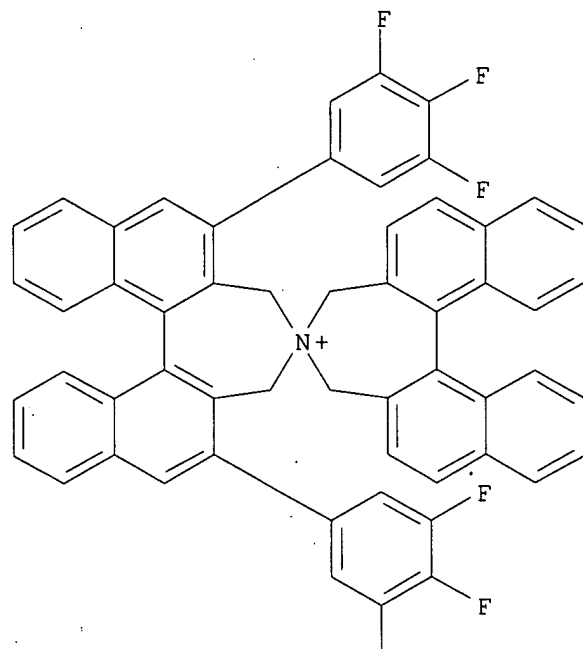
IT 287384-12-7 438002-03-0 503538-60-1

RL: CAT (Catalyst use); USES (Uses) .

(asym. synthesis of tertiary N-aryl  $\alpha$ -hydroxy amides and their derivs. by quaternary ammonium salt-catalyzed phase-transfer alkylation of diaryl oxazolidinediones)

RN 287384-12-7 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
 2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bS)- (CA INDEX  
 NAME)

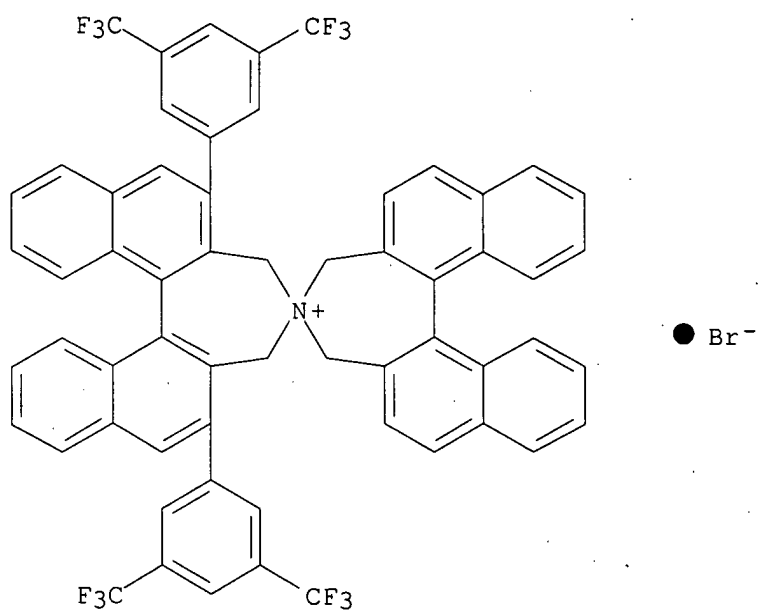
PAGE 1-A



PAGE 2-A

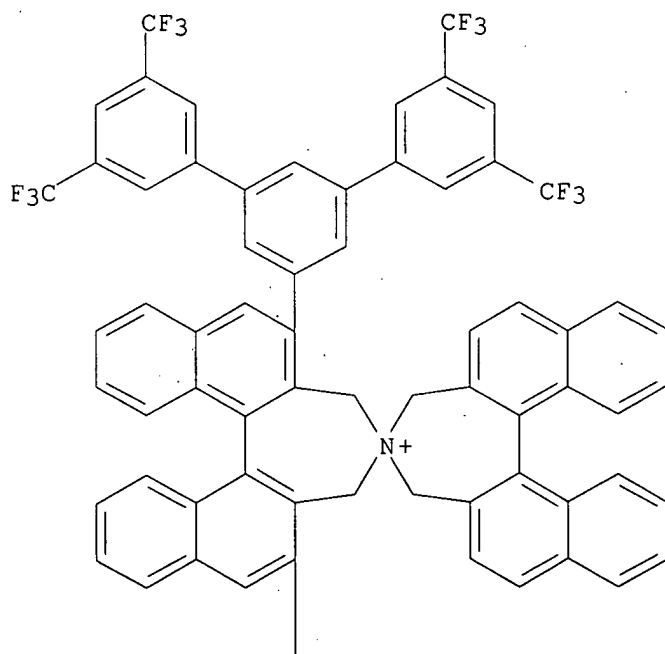


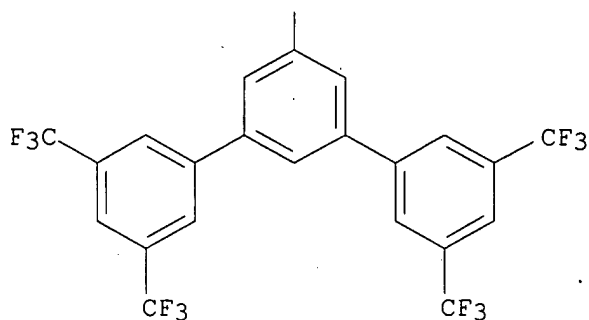
RN 438002-03-0 CAPLUS  
 CN 8,8'-Spirobi[8H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-  
 bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide (1:1),  
 (11bS,11'bS)- (CA INDEX NAME)



RN 503538-60-1 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[3,3'',5,5''-tetrakis(trifluoromethyl)[1,1':3',1''-terphenyl]-5'-yl]-, bromide (1:1), (11bS,11'bs)- (CA INDEX NAME)

PAGE 1-A





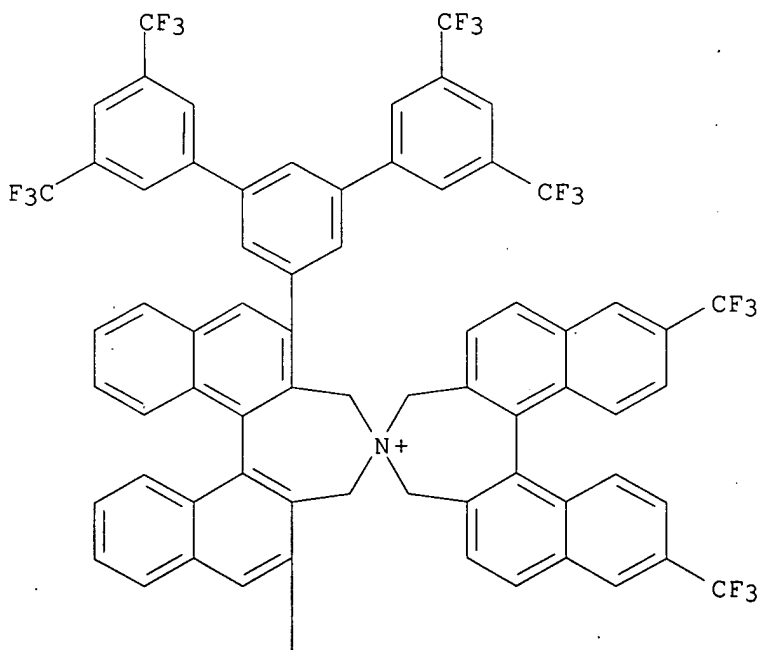
IT 905708-29-4P 905708-30-7P

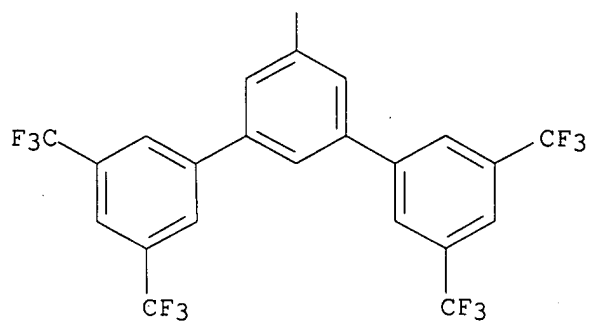
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
USES (Uses)

(asym. synthesis of tertiary N-aryl  $\alpha$ -hydroxy amides and their  
derivs. by quaternary ammonium salt-catalyzed phase-transfer alkylation  
of diaryl oxazolidinediones)

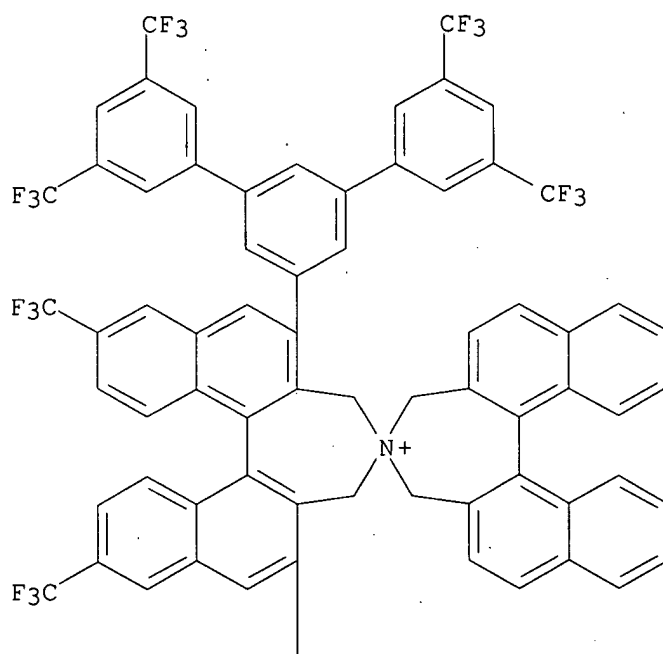
RN 905708-29-4 CAPLUS

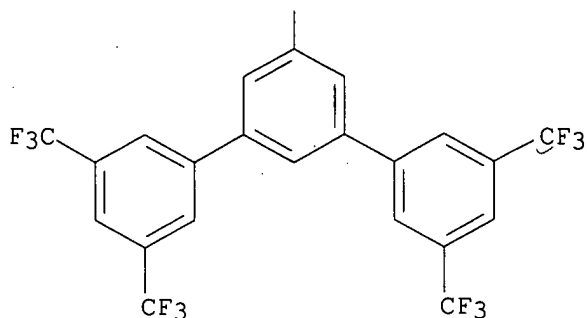
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,3'',5,5''-  
tetrakis(trifluoromethyl)[1,1':3',1''-terphenyl]-5'-yl]-9',14''-  
bis(trifluoromethyl)-, bromide, (11bS,11'bS)- (9CI) (CA INDEX NAME)





RN 905708-30-7 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,3'',5,5''-  
 tetrakis(trifluoromethyl)[1,1':3',1''-terphenyl]-5'-yl]-9,14-  
 bis(trifluoromethyl)-, bromide, (11bS,11'bS)- (9CI) (CA INDEX NAME)





REFERENCE COUNT: 48 THERE ARE 48 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 15 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2006:315235 CAPLUS

DOCUMENT NUMBER: 145:8414

TITLE: Highly enantioselective monoalkylation of p-chlorobenzaldehyde imine of glycine tert-butyl ester under mild phase-transfer conditions

AUTHOR(S): Ooi, Takashi; Arimura, Yuichiro; Hiraiwa, Yukihiro; Yuan, Lin Ming; Kano, Taichi; Inoue, Toru; Matsumoto, Jun; Maruoka, Keiji

CORPORATE SOURCE: Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto, 606-8502, Japan

SOURCE: Tetrahedron: Asymmetry (2006), 17(4), 603-606

CODEN: TASYE3; ISSN: 0957-4166

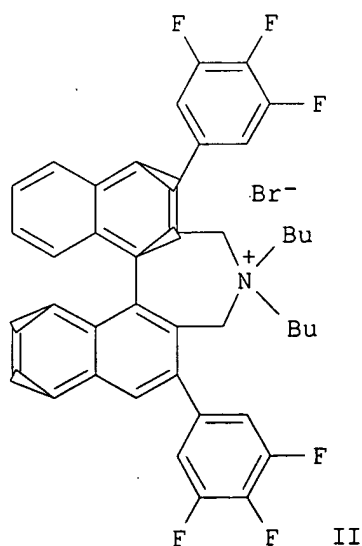
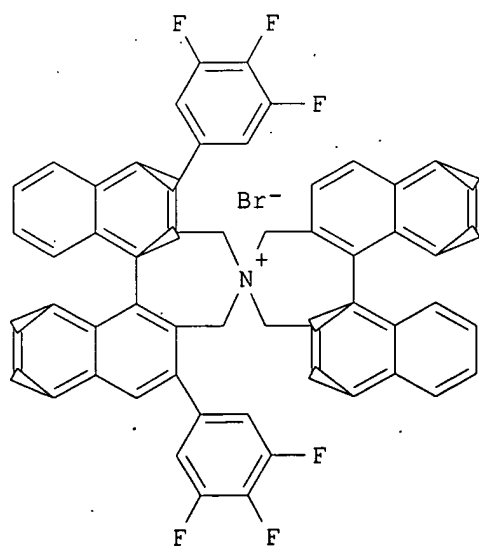
PUBLISHER: Elsevier B.V.

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 145:8414

GI



AB The selective monoalkylation of glycine tert-Bu ester aldimine Schiff

base, 4-ClC<sub>6</sub>H<sub>4</sub>CH:NCH<sub>2</sub>CO<sub>2</sub>Bu-t, was accomplished with high yields and excellent enantioselectivity under mild liquid-liquid phase-transfer conditions by the use of binaphthyl-derived chiral quaternary ammonium bromides (R,R)-I and (R)-II as catalysts. For example, 4-ClC<sub>6</sub>H<sub>4</sub>CH:NCH<sub>2</sub>CO<sub>2</sub>Bu-t was alkylated with 1-naphthylmethyl bromide in presence of catalyst (R)-II to afford (S)-2-amino-3-(1-naphthyl)propanoic acid tert-Bu ester in 96% yield with 99% enantiomeric excess. Thus, the above glycinate Schiff base can be used as a cost-effective substrate to synthesize optically active  $\alpha$ -alkyl- $\alpha$ -amino acid derivs. by chiral phase-transfer catalysis.

IT 534570-50-8

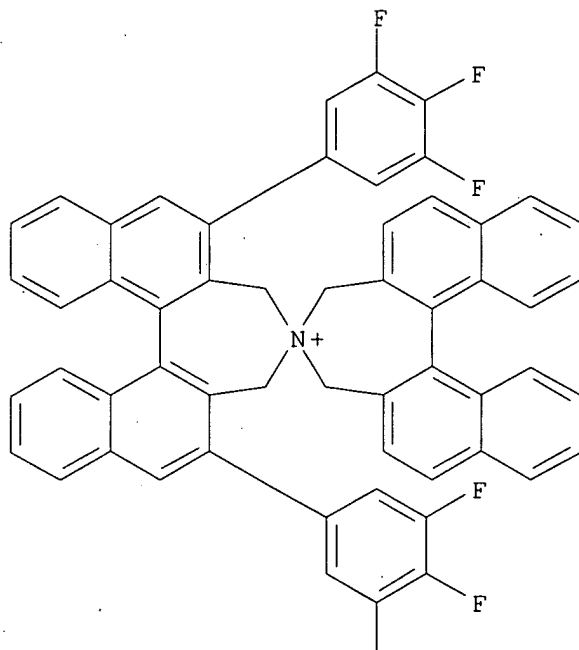
RL: CAT (Catalyst use); USES (Uses)

(enantioselective monoalkylation of glycinate Schiff base using alkyl halides with quaternary ammonium bromide as phase-transfer catalysts)

RN 534570-50-8 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bR,11'bR)- (CA INDEX NAME)

PAGE 1-A



PAGE 2-A



● Br<sup>-</sup>

REFERENCE COUNT:

14

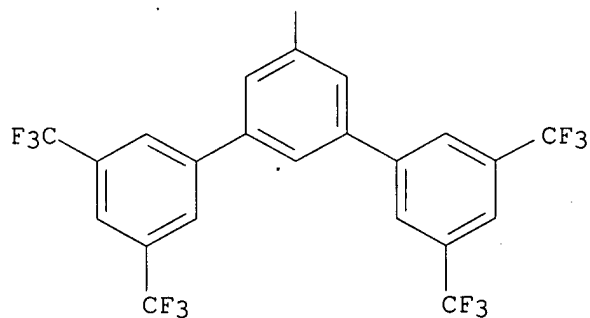
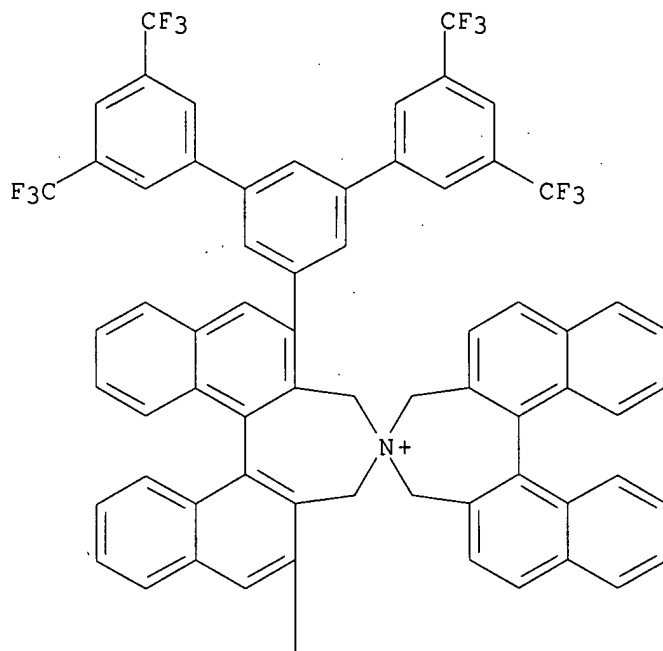
THERE ARE 14 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 16 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2005:1299314 CAPLUS

DOCUMENT NUMBER: 144:192295  
TITLE: Asymmetric Michael addition of silyl nitronates to cyclic  $\alpha,\beta$ -unsaturated ketones catalyzed by chiral quaternary ammonium bifluorides: isolation and selective functionalization of enol silyl ethers of optically active  $\gamma$ -nitro ketones  
AUTHOR(S): Ooi, Takashi; Doda, Kanae; Takada, Saki; Maruoka, Keiji  
CORPORATE SOURCE: Department of Chemistry, Graduate School of Science, Kyoto University Sakyo, Kyoto, 606-8502, Japan  
SOURCE: Tetrahedron Letters (2005), Volume Date 2006, 47(2), 145-148  
CODEN: TELEAY; ISSN: 0040-4039  
PUBLISHER: Elsevier B.V.  
DOCUMENT TYPE: Journal  
LANGUAGE: English  
OTHER SOURCE(S): CASREACT 144:192295  
AB Highly enantioselective Michael addition of silyl nitronates to cyclic  $\alpha,\beta$ -unsatd. ketones was accomplished using N-spiro C2-sym. chiral quaternary ammonium bifluoride as an efficient catalyst, offering a new route to the enol silyl ethers of optically active  $\gamma$ -nitro ketones. The synthetic utility of this transformation was demonstrated by the diastereoselective derivations of the optically active enol silyl ethers to the corresponding  $\alpha$ -substituted cyclic ketones having three consecutive stereochem. defined stereocenters.  
IT 503538-65-6 586344-91-4  
RL: CAT (Catalyst use); USES (Uses)  
(asym. Michael addition of silyl nitronates to cyclic unsatd. ketones catalyzed by chiral ammonium bifluorides to give enol silyl ethers of optically active  $\gamma$ -nitro ketones)  
RN 503538-65-6 CAPLUS  
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[3,3'',5,5''-tetrakis(trifluoromethyl)[1,1':3',1''-terphenyl]-5'-yl]-, (11bS,11'bS)-, (hydrogen difluoride) (9CI) (CA INDEX NAME)  
CM 1  
CRN 503538-64-5  
CMF C88 H48 F24 N

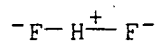




CM 2

CRN 18130-74-0

CMF F2 H



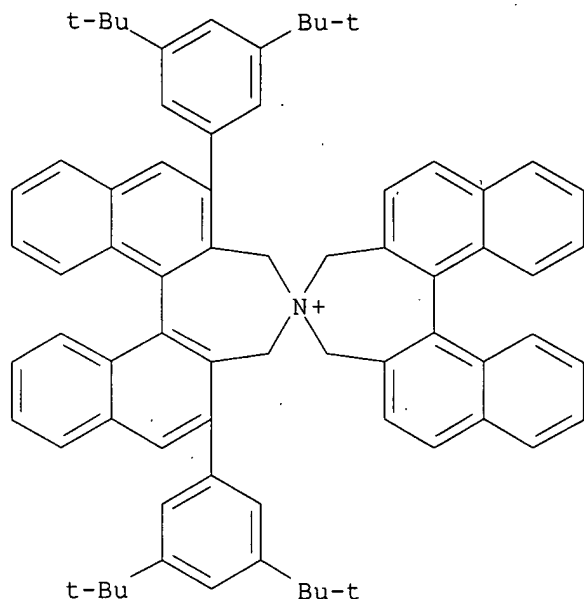
RN 586344-91-4 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(1,1-dimethylethyl)phenyl]-3,3',5,5'-tetrahydro-, (11bR,11'bR)-, (hydrogen difluoride) (1:1) (CA INDEX NAME)

CM 1

CRN 586344-90-3

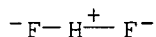
CMF C72 H72 N



CM 2

CRN 18130-74-0

CMF F2 H



REFERENCE COUNT: 16 THERE ARE 16 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 17 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2005:1122413 CAPLUS

DOCUMENT NUMBER: 144:51242

TITLE: N-spiro chiral quaternary ammonium bromide catalyzed diastereo- and enantioselective conjugate addition of nitroalkanes to cyclic  $\alpha,\beta$ -unsaturated ketones under phase-transfer conditions

AUTHOR(S): Ooi, Takashi; Takada, Saki; Fujioka, Shingo; Maruoka, Keiji

CORPORATE SOURCE: Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto, Sakyo, 606-8502, Japan

SOURCE: Organic Letters (2005), 7(23), 5143-5146

CODEN: ORLEF7; ISSN: 1523-7060

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 144:51242

AB Conjugate addition of various prochiral nitroalkanes to cyclic  $\alpha,\beta$ -unsatd. ketones was efficiently catalyzed by N-spiro C2-sym. chiral quaternary ammonium bromide possessing a 3,5-bis(3,4,5-trifluorophenyl)phenyl substituent, under solid-liquid phase-transfer conditions to afford  $\gamma$ -nitro ketones in excellent chemical yields with unprecedented levels of diastereo- and enantiocontrol.

IT 287384-12-7 503538-60-1 871130-09-5

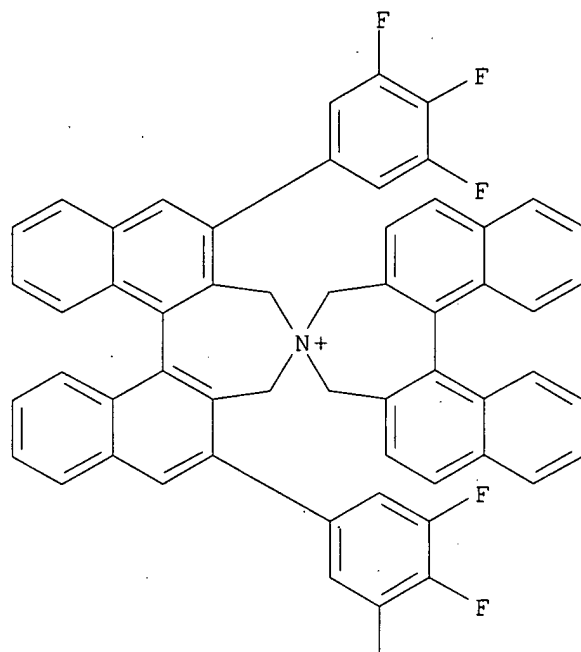
RL: CAT (Catalyst use); USES (Uses)

(N-spiro chiral quaternary ammonium bromide-catalyzed stereoselective conjugate addition of nitroalkanes to cyclic  $\alpha,\beta$ -unsatd. ketones under phase transfer conditions)

RN 287384-12-7 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)

PAGE 1-A

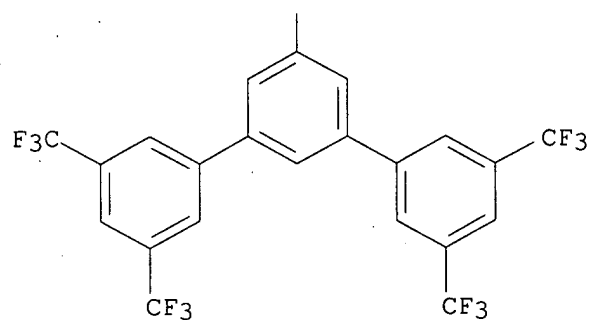
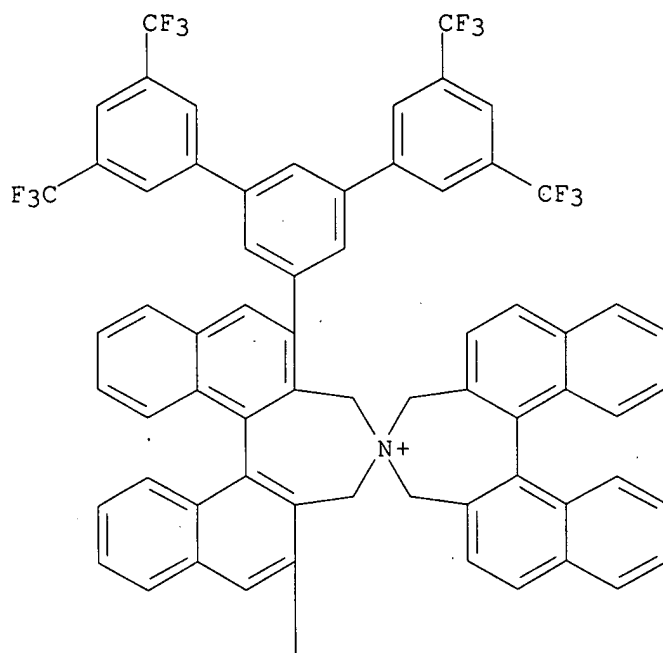


PAGE 2-A

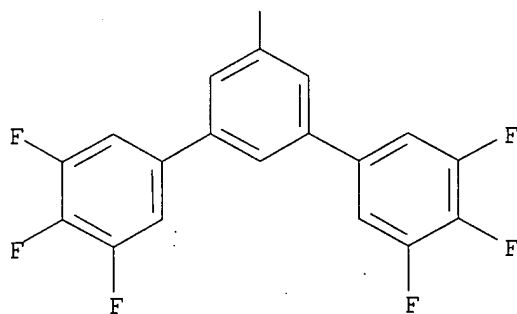
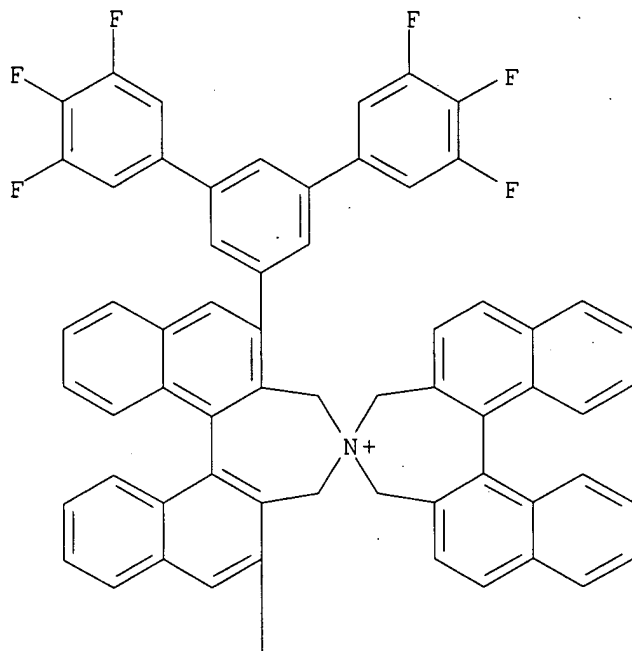


RN 503538-60-1 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[3,3',5,5'-tetrakis(trifluoromethyl)[1,1':3',1''-terphenyl]-5'-yl]-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



RN 871130-09-5 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis(3,3'',4,4'',5,5''-hexafluoro[1,1':3',1''-terphenyl]-5'-yl)-3,3',5,5'-tetrahydro-, bromide, (11bS,11'bs)- (9CI) (CA INDEX NAME)



REFERENCE COUNT: 29 THERE ARE 29 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

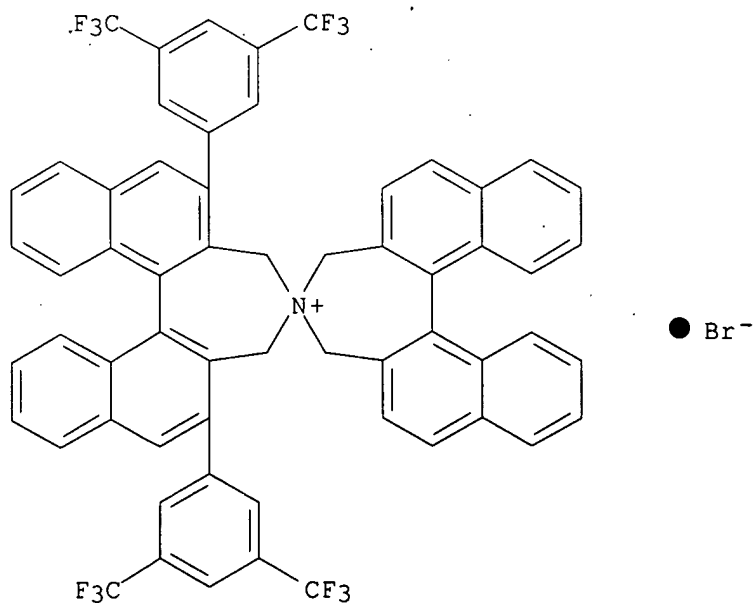
L3 ANSWER 18 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2005:1048699 CAPLUS  
 DOCUMENT NUMBER: 143:346808  
 TITLE: Preparation of optically-active 3-nitroalkylmalonate esters  
 INVENTOR(S): Maruoka, Keiji; Oi, Takashi  
 PATENT ASSIGNEE(S): Nagase & Co., Ltd., Japan  
 SOURCE: Jpn. Kokai Tokkyo Koho, 39 pp.  
 CODEN: JKXXAF  
 DOCUMENT TYPE: Patent  
 LANGUAGE: Japanese  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 2005263664	A	20050929	JP 2004-76692	20040317
PRIORITY APPLN. INFO.:			JP 2004-76692	20040317
OTHER SOURCE(S):	MARPAT 143:346808			

GI

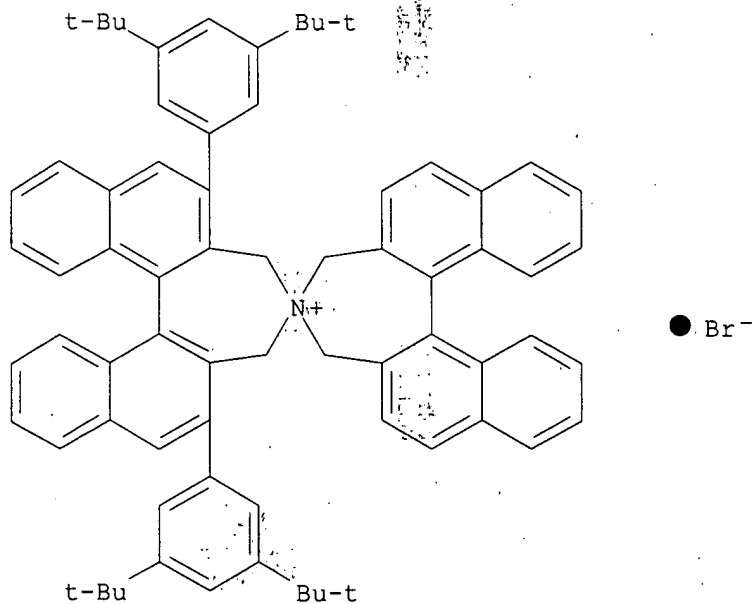
\* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT \*

- AB Optically-active  $O_2NCHR_1CHR_2CH(CO_2R_3)(CO_2R_4)$  ( $R_1, R_2 = H, C_1-8$  alkyl optionally substituted with  $C_1-8$  alkoxy, (hetero)aryl, (hetero)aralkyl, optionally substituted with  $C_1-4$  alkyl, cyano, halo, amino, etc.;  $R_3, R_4 = H, C_1-6$  alkyl, aryl, aralkyl optionally substituted with  $C_1-4$  alkyl or  $C_1-5$  alkoxy), useful as intermediates for optically-active amino acids, are prepared by reacting  $R_1CH_2NO_2$  ( $R_1 =$  same as above) with  $R_2CH:C(CO_2R_3)(CO_2R_4)$  with  $R_2N:CHCO_2R_3$  ( $R_2-R_4 =$  same as above) in solvents containing inorg. bases in the presence of optically-active cyclic quaternary ammonium salts I [ $R_5, R_6 = C_1-8$  (halo)alkyl,  $C_2-8$  (halo)alkenyl,  $C_2-8$  (halo)alkynyl, (hetero)aryl, (hetero)aralkyl, optionally substituted with  $C_1-4$  (halo)alkyl, cyano, amino, etc.;  $Y, Z = H$ , monovalent organic group or  $Y$  and  $Z$  are bonded together to form divalent organic group;  $X =$  halo]. Thus, a mixture of  $PrNO_3$ ,  $PhCH:C(CO_2CHMe_2)_2$ , a catalyst II (preparation given), and  $Cs_2CO_3$  was vigorously stirred at  $0^\circ$  for 6 h to give 99% optically-active  $O_2NCHEtCHPhCH(CO_2CHMe_2)_2$  (anti/syn ratio = 86:14).
- IT 438002-03-0P 501934-20-9P 503538-60-1P  
 RL: CAT (Catalyst use); IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
 (preparation of optically-active 3-nitroalkylmalonate esters from nitro compds. and ylidenemalonates using optically-active cyclic quaternary ammonium salts as catalysts)
- RN 438002-03-0 CAPLUS
- CN 8,8'-Spirobi[8H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



RN 501934-20-9 CAPLUS

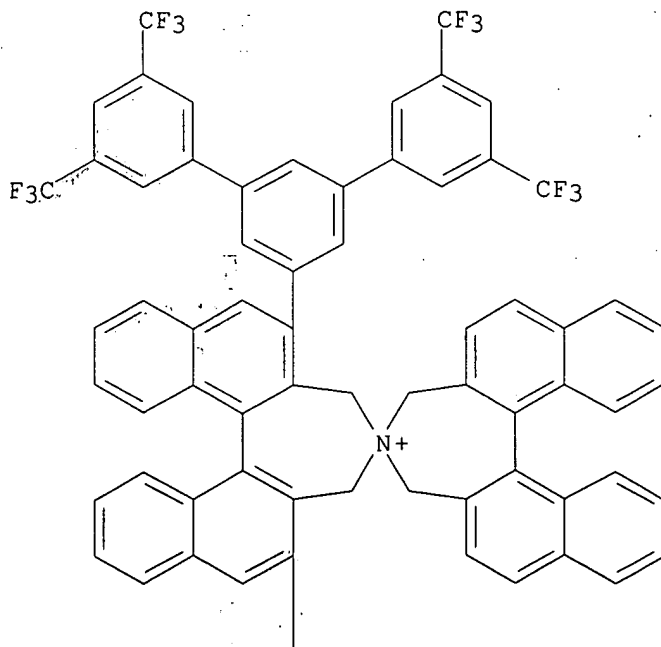
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(1,1-dimethylethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)

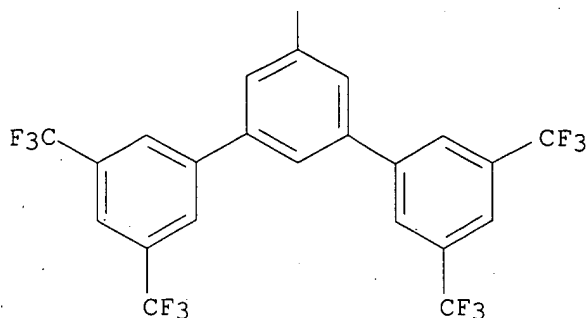


RN 503538-60-1 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[3,3',5,5'-tetrakis(trifluoromethyl)[1,1':3',1''-terphenyl]-5'-yl]-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)

PAGE 1-A

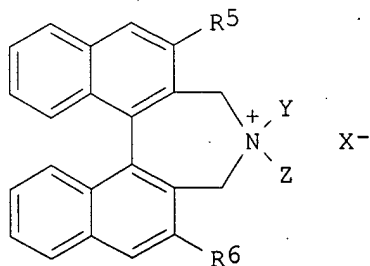




● Br<sup>-</sup>

L3 ANSWER 19 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2005:1023434 CAPLUS  
 DOCUMENT NUMBER: 143:326628  
 TITLE: Preparation of optically-active 3-aminoaspartic acid derivatives by reacting Schiff bases of glycines with  $\alpha$ -imino esters using optically-active quaternary ammonium salts  
 INVENTOR(S): Maruoka, Keiji; Oi, Takashi  
 PATENT ASSIGNEE(S): Nagase & Co., Ltd., Japan  
 SOURCE: Jpn. Kokai Tokkyo Koho, 47 pp.  
 CODEN: JKXXAF  
 DOCUMENT TYPE: Patent  
 LANGUAGE: Japanese  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 2005255610	A	20050922	JP 2004-68812	20040311
PRIORITY APPLN. INFO.:			JP 2004-68812	20040311
OTHER SOURCE(S):	MARPAT 143:326628			
GI				



I

AB Optically-active  $R_1OCHOCH(NH_2)CH(NHR_2)CO_2R_3$  ( $R_1$ - $R_3$  = H, C1-8 alkyl optionally substituted with C1-8 alkoxy, (hetero)aryl, (hetero)aralkyl, optionally substituted with C1-4 alkyl, cyano, halo, amino, etc.), useful as chiral catalysts, precursors for antitumor or antibiotic streptolidine lactam, etc., are prepared by reacting  $Ph_2C:NCCH_2CO_2R_1$  ( $R_1$  = same as above) with  $R_2N:CHCO_2R_3$  ( $R_2$ ,  $R_3$  = same as above) in the presence of optically-active quaternary ammonium salts I [ $R_5$ ,  $R_6$  = C1-8 (halo)alkyl, C2-8 (halo)alkenyl, C2-8 (halo)alkynyl, (hetero)aryl, (hetero)aralkyl,



optionally substituted with C1-4 (halo)alkyl, cyano, amino, etc.; Y, Z = H, monovalent organic group or Y and Z are bonded together to form divalent organic group; X = halo]. Thus, p-MeOC6H4N:CHCO2Et was added dropwise to a mixture of mesitylene, an aqueous NaOH solution, Ph2C:NCH2CO2CMe3, and a catalyst

II at -20° and the reaction mixture was vigorously stirred at -20° for 6 h to give 88% diastereomeric mixture of (2S,3S)-1-tert-Bu 4-Et 3-N-(4-methoxyphenyl)aminoaspartate (syn/anti = 4.5:1). This was further processed to give a precursor of antitumor or antibiotic streptolidine lactam.

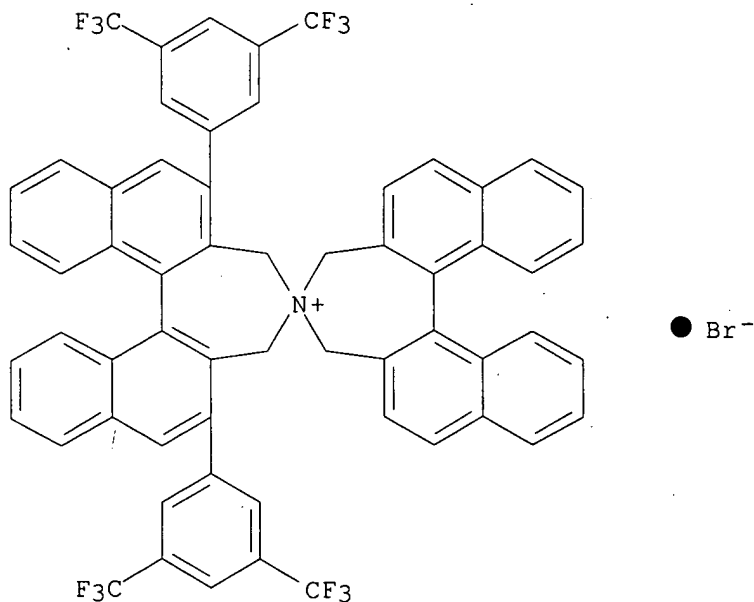
IT 515137-97-0 534570-50-8 736974-91-7

RL: CAT (Catalyst use); USES (Uses)

(preparation of optically-active 3-aminoaspartic acid derivs. by reacting Schiff bases of glycines with α-imino esters using optically-active quaternary ammonium salts)

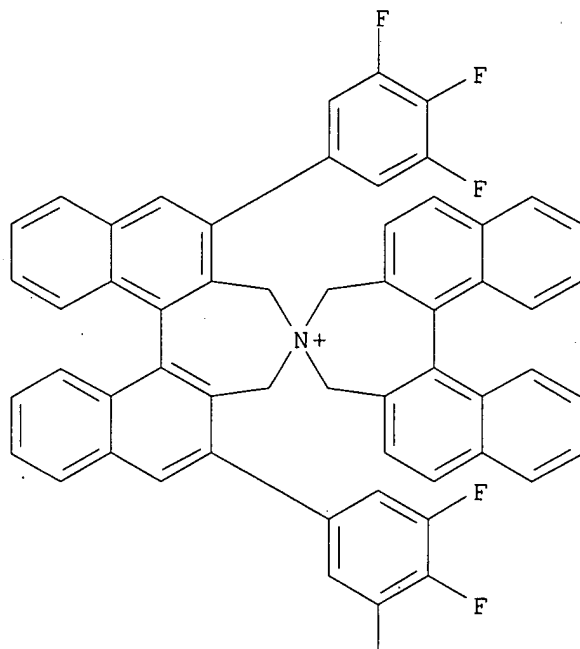
RN 515137-97-0 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide (1:1), (11bR,11'bR)- (CA INDEX NAME)

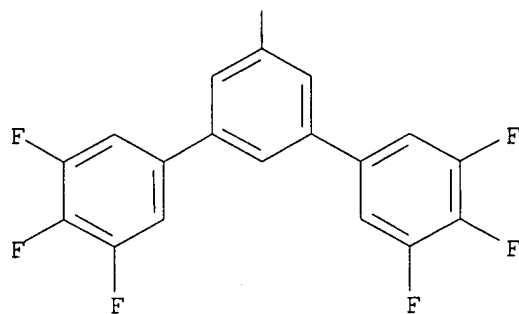
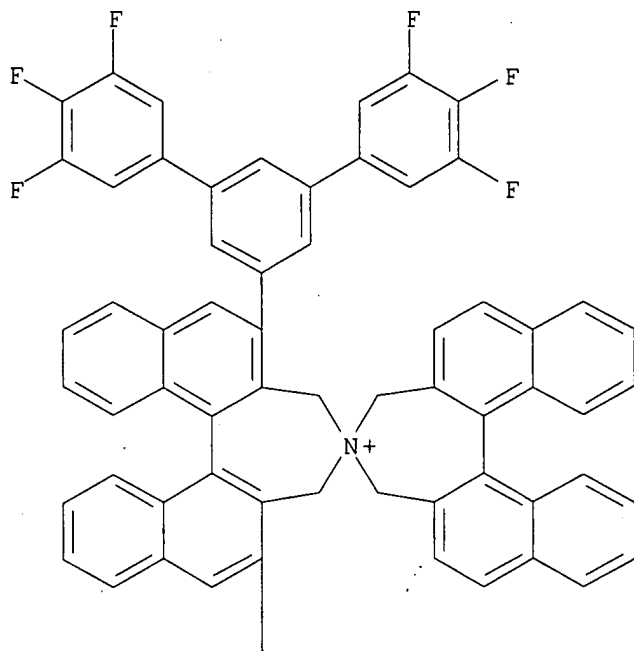


RN 534570-50-8 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bR,11'bR)- (CA INDEX NAME)



RN 736974-91-7 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-  
 bis(3,3'',4,4'',5,5''-hexafluoro[1,1':3',1''-terphenyl]-5'-yl)-3,3',5,5'-  
 tetrahydro-, bromide, (11bR,11'bR)- (9CI) (CA INDEX NAME)



L3 ANSWER 20 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2005:960134 CAPLUS

DOCUMENT NUMBER: 143:248660

TITLE: Preparation of Schiff bases of substituted amino acid amides and optically-active vicinal diamines by hydrolysis and reduction of the Schiff bases

INVENTOR(S): Maruoka, Keiji; Oi, Takashi

PATENT ASSIGNEE(S): Nagase & Co., Ltd., Japan

SOURCE: Jpn. Kokai Tokkyo Koho, 50 pp.

CODEN: JKXXAF

DOCUMENT TYPE: Patent

LANGUAGE: Japanese

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 2005232103	A	20050902	JP 2004-44771	20040220
PRIORITY APPLN. INFO.:			JP 2004-44771	20040220
OTHER SOURCE(S):	MARPAT 143:248660			
GI				

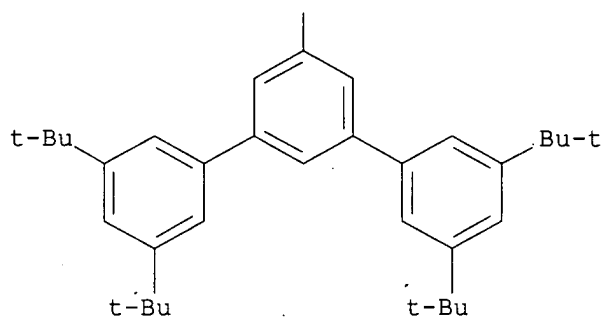
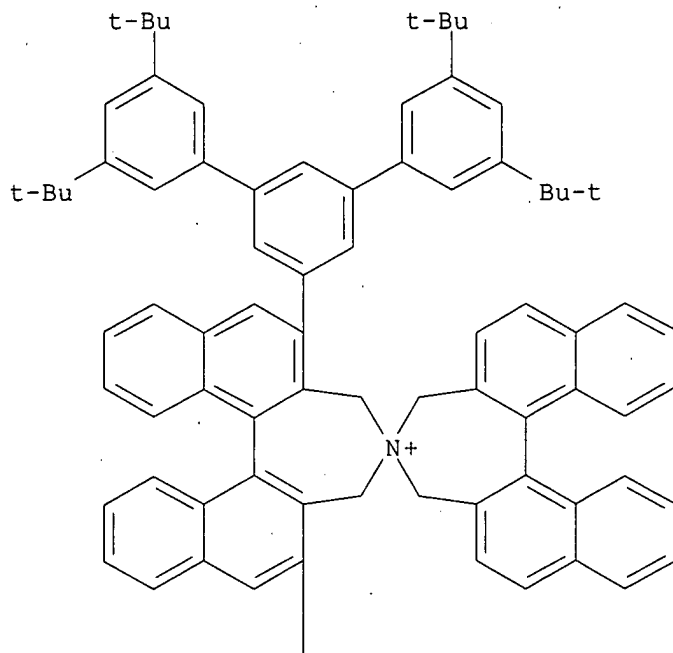
\* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT \*

AB R4R5C:NCR3R6CONHCHR1R2 [I; R1, R2 = H, C1-4 (halo)alkyl, C1-3 (halo)alkoxy, (halo)aryl; R3 = H, C1-8 (halo)alkyl, C2-8 (halo)alkenyl, C2-8 (halo)alkynyl, (hetero)aralkyl optionally substituted with halo, C1-4 (halo)alkyl, etc.; if R3 = H, then R4 = aryl optionally substituted with C1-4 (halo)alkyl, C1-3 (halo)alkyl, or halo; if R3 ≠ H, then R4 = H; R5 = C1-4 (halo)alkyl, C1-3 (halo)alkoxy, (halo)aryl; R6 = C1-8 alkyl, C2-8 alkenyl, aralkyl optionally substituted with C1-4 alkyl] are prepared by reacting I (R1-R5 = same as above; R6 = H) with organic halides in the presence of phase-transfer catalysts, e.g. quaternary ammonium salts, e.g. Bu4NBr, N-spiro quaternary ammonium salts II [R7, R8 = H, C1-7 (halo)alkyl, C2-6 (halo)alkenyl, (un)substituted (hetero)aryl, N,N-di(C1-4 alkyl)carbamoyl, etc.; X = Cl, Br, I] or III [R7, R8, X = same as above; R11-R41 = H, C1-6 alkyl, halo, (un)substituted (hetero)aryl, carbamoyl, etc.]. Optically-active H2NCR3R6CH2NHCHR1R2 (R1, R2, R3, R6 = same as above), useful as intermediates for drugs, asym. catalyst ligands, chiral chiral auxiliaries, etc., are prepared by hydrolysis and reduction of the above Schiff bases. Thus, a mixture of Ph2C:NCH2CONHCHPh2 (preparation given), optically-active II [R7 = R8 = 3,5-bis(3,5-di-tert-butyl-phenyl)phenyl, X = Br], KOH, PhCH2Br, and toluene at 0° for 3 h to give 98% optically-active Ph2C:NCH(CH2Ph)CONHCHPh2 (92% e.e.), which was hydrolyzed with HCl for deprotection and reduced with LiAlH4 to give 96% optically-active H2NCH(CH2Ph)CH2NHCHPh2.

IT 501934-21-0  
 RL: CAT (Catalyst use); USES (Uses)  
 (α-alkylation of amino acid amide Schiff bases with organic halides and phase-transfer catalysts, and hydrolysis and reduction of the products to give optically-active vicinal diamines)

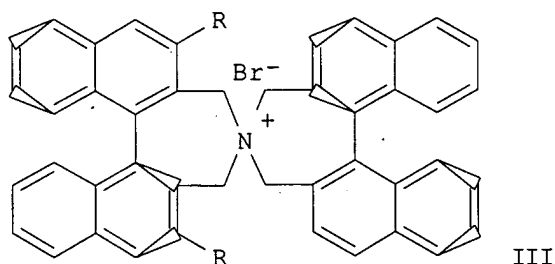
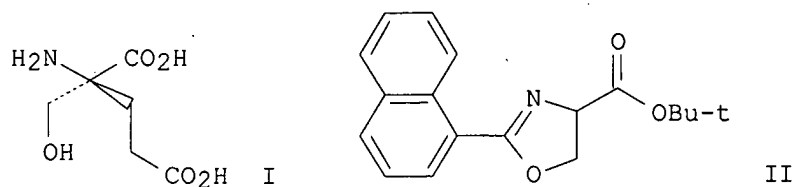
RN 501934-21-0 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[3,3'',5,5''-tetrakis(1,1-dimethylethyl)[1,1':3',1''-terphenyl]-5'-yl]-, bromide (1:1), (11bS,11'bs)- (CA INDEX NAME)



L3 ANSWER 21 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2005:562306 CAPLUS  
 DOCUMENT NUMBER: 143:230159  
 TITLE: Highly Enantioselective Synthesis of  
 (2S)- $\alpha$ -(Hydroxymethyl)-glutamic Acid by the  
 Catalytic Michael Addition of 2-Naphthalen-1-yl-2-  
 oxazoline-4-carboxylic Acid tert-Butyl Ester  
 AUTHOR(S): Lee, Yeon-Ju; Lee, Jihye; Kim, Mi-Jeong; Jeong,  
 Byeong-Seon; Lee, Jeong-Hee; Kim, Taek-Soo; Lee,  
 Jihoon; Ku, Jin-Mo; Jew, Sang-sup; Park, Hyeung-geun  
 CORPORATE SOURCE: Research Institute of Pharmaceutical Sciences and  
 College of Pharmacy, Seoul National University, Seoul,  
 151-742, S. Korea  
 SOURCE: Organic Letters (2005), 7(15), 3207-3209  
 CODEN: ORLEF7; ISSN: 1523-7060

PUBLISHER: American Chemical Society  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 OTHER SOURCE(S): CASREACT 143:230159  
 GI



AB Highly enantioselective synthesis of (2S)- $\alpha$ -(hydroxymethyl)-glutamic acid (I) was accomplished by the catalytic Michael addition of 2-(naphthalen-1-yl)-2-oxazoline-4-carboxylic acid tert-Bu ester (II), using phosphazene base BEMP in CH<sub>2</sub>Cl<sub>2</sub> at -60° in the presence of (S)-binaphthyl quaternary ammonium salt III (R = 3,4,5-trifluorophenyl) as the phase transfer catalyst.

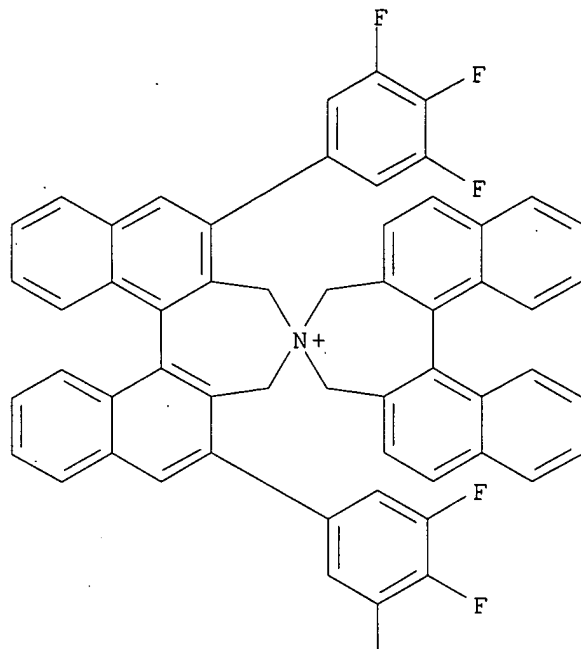
IT 287384-12-7

RL: CAT (Catalyst use); USES (Uses)

(enantioselective preparation of (hydroxymethyl)glutamic acid by phase transfer catalytic Michael reaction of (aryl)oxazolinecarboxylate with acrylate)

RN 287384-12-7 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)

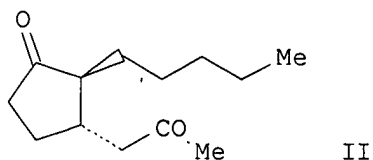


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F

● Br<sup>-</sup>

REFERENCE COUNT: 32 THERE ARE 32 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 22 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2005:412162 CAPLUS  
 DOCUMENT NUMBER: 144:6604  
 TITLE: Enantioselective synthesis of the fragrance trans-magnolione under asymmetric phase transfer catalysis  
 AUTHOR(S): Superchi, Stefano; Nardiello, Mariangela; Donnoli, Maria Irene; Scafato, Patrizia; Menicagli, Rita; Rosini, Carlo  
 CORPORATE SOURCE: Dipartimento di Chimica, Universita della Basilicata, Potenza, 85100, Italy  
 SOURCE: Comptes Rendus Chimie (2005), 8(5), 867-874  
 CODEN: CRCOCR; ISSN: 1631-0748  
 PUBLISHER: Editions Scientifiques et Medicales Elsevier  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 OTHER SOURCE(S): CASREACT 144:6604  
 GI



AB The stereoselective synthesis of the fragrance trans-magnolione via conjugate Michael addition of alkyl acetoacetates to 2-pentyl-2-cyclopentenone (I) under solid/liquid phase transfer catalysis (PTC) was reported. Under optimized conditions, the 1,4-addition of tert-Bu acetoacetate to enone I catalyzed by N1-(9-anthracenylmethyl)quininium chloride afforded, after hydrolysis and decarboxylation, (2S,3S)-trans-magnolione (II) with 85/15 trans/cis d.r. and 74% ee. The use of the pseudo-enantiomeric catalyst N1-(9-anthracenylmethyl)quinidinium chloride gave (2R,3R)-trans-magnolione with comparable enantio- and diastereoselectivity.

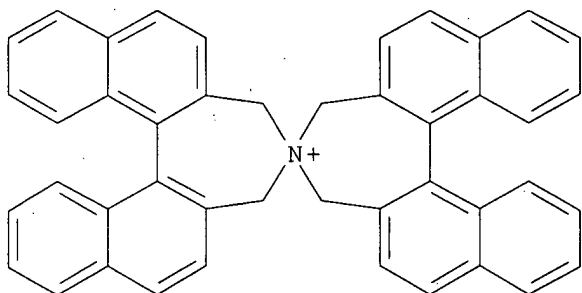
IT 237762-40-2P

RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)

(enantioselective synthesis of the fragrance trans-magnolione via stereoselective Michael addition mediated by chiral phase transfer catalysts)

RN 237762-40-2 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



● Br<sup>-</sup>

REFERENCE COUNT: 29 THERE ARE 29 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 23 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2005:395254 CAPLUS

DOCUMENT NUMBER: 142:430529

TITLE: Process for production of asymmetric alkyl compounds with alkali-treated solid carrier and alkali-treated solid carrier to be used in the process

INVENTOR(S): Koshima, Hideko; Yu, Haitao

PATENT ASSIGNEE(S): Japan Science and Technology Agency, Japan

SOURCE: PCT Int. Appl., 47 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: Japanese

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:



PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005040096	A1	20050506	WO 2004-JP7393	20040528
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW, RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
EP 1693362	A1	20060823	EP 2004-745429	20040528
R: DE, FR, GB				
US 20070225157	A1	20070927	US 2007-576682	20070116
PRIORITY APPLN. INFO.:			JP 2003-364982	A 20031024
			WO 2004-JP7393	W 20040528

OTHER SOURCE(S): CASREACT 142:430529; MARPAT 142:430529

AB A process for the production of asym. alkyl compds., i.e. optically active amino acid derivs., which is characterized by comprising the step of mixing a reaction solution containing a glycine imine ester, an alkyl halide,

and

an asym. catalyst having an ability to make asym. synthesis proceed with an alkali-treated solid carrier obtained by treating a solid carrier made of an inorg. compound with an alkaline substance to thereby conduct an asym. synthesis reaction. On allowing the obtained mixture to stand at room temperature, the asym. alkylation between the glycine imine ester and the alkyl halide catalyzed by the asym. catalyst (cinchonine or cinchonidine compound) is accomplished on the alkali-treated solid carrier in about one hour to give an asym. alkyl compound having a high optical purity in a high yield. The process can dispense with the stirring of a solvent and enables efficient and stable accomplishment of asym. alkylation in a short time and high-yield synthesis of an asym. alkyl compound having a high optical purity. Microwave irradiation of alkali treated solid increases the rate of asym. alkylation by .apprx.ten-fold and thus shortens reaction time. Thus, 3 g kaolin was added 25% aqueous KOH solution, irradiated by ultrasound

at

42 kHz for 4 h, and filtered under reduced pressure. The solid obtained was irradiated in a 500 W microwave oven at 2.45 GHz for 15 min, and then pulverized by a mortar to give a KOH-treated kaolin (kaolin/KOH) catalyst. Thus, the kaolin/KOH catalyst (0.51 g) was added to a solution of N-(dimethylmethyleneglycine tert-Bu ester 0.05, HCD-allyl (CAS REG Number 480427-57-4) 0.005, and benzyl bromide 0.084 mmol in a 6:4 mixture of toluene and CHCl<sub>3</sub> (6:4) (0.15 mL) and the resulting mixture was left to stand at room temperature for 60 min to give 99% N-(dimethylmethyleneglycine)-L-phenylalanine tert-Bu ester (92% optical purity).

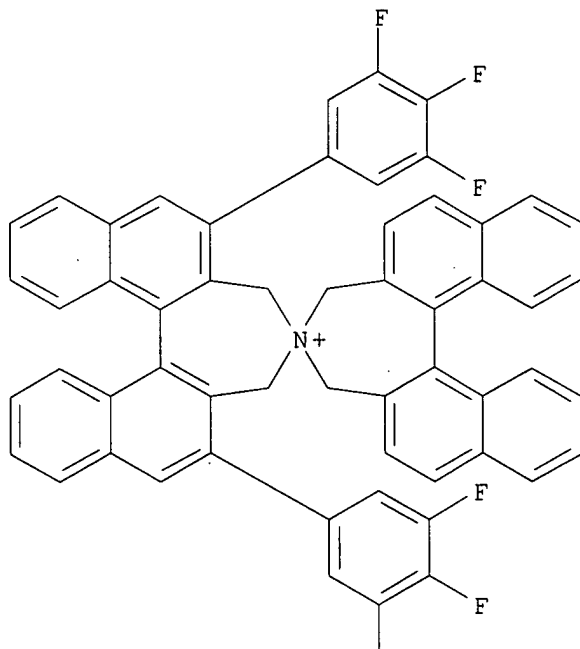
IT 287384-12-7

RL: CAT (Catalyst use); USES (Uses)

(preparation of optically active amino acid derivs. by asym. alkylation of glycine imine ester with alkyl halide using alkali-treated solid carrier and cinchonine or cinchonidine compound)

RN 287384-12-7 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)

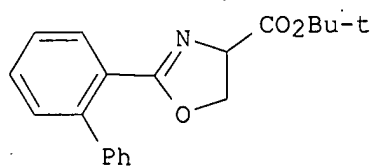


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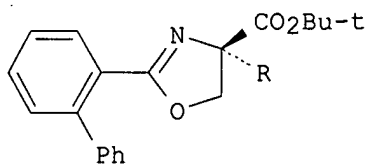
● Br<sup>-</sup>

REFERENCE COUNT: 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 24 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2005:245636 CAPLUS  
 DOCUMENT NUMBER: 142:463641  
 TITLE: Highly Enantioselective Synthesis of  
 (R)- $\alpha$ -Alkylserines via Phase-Transfer Catalytic  
 Alkylation of o-Biphenyl-2-oxazoline-4-carboxylic Acid  
 tert-Butyl Ester Using Cinchona-Derived Catalysts  
 AUTHOR(S): Lee, Yeon-Ju; Lee, Jihye; Kim, Mi-Jeong; Kim,  
 Taek-Soo; Park, Hyeung-geun; Jew, Sang-sup  
 CORPORATE SOURCE: Research Institute of Pharmaceutical Sciences and  
 College of Pharmacy, Seoul National University, Seoul,  
 151-742, S. Korea  
 SOURCE: Organic Letters (2005), 7(8), 1557-1560  
 CODEN: ORLEF7; ISSN: 1523-7060  
 PUBLISHER: American Chemical Society  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 OTHER SOURCE(S): CASREACT 142:463641  
 GI



I



II

AB This work describes the asym. alkylation of o-biphenyl-2-oxazoline-4-carboxylic acid tert-Bu ester (I) using cinchona-derived phase-transfer catalyst N(1)-(9-anthracenylmethyl)-O(9)-allyl-dihydrocinchonidinium bromide to give (4R)-alkyloxazolinecarboxylates II in yields  $\geq 75\%$  with enantiomeric excess  $\geq 90\%$ . (R)-Alkylserines can be obtained from II via acidic hydrolysis.

IT 287384-12-7

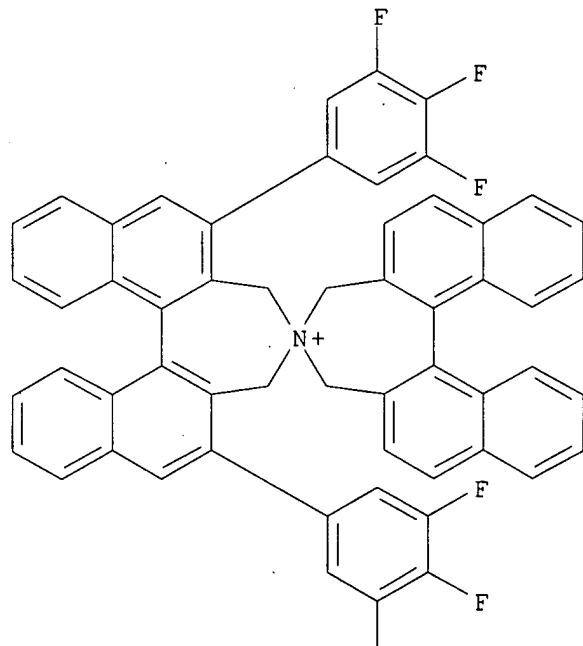
RL: CAT (Catalyst use); USES (Uses)

(using cinchona-derived phase-transfer catalysts for asym. alkylations of aryloxazolinecarboxylic acid esters as protected serine derivs.)

RN 287384-12-7 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)

PAGE 1-A



PAGE 2-A

F

● Br<sup>-</sup>

REFERENCE COUNT: 25 THERE ARE 25 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 25 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2005:241622 CAPLUS

DOCUMENT NUMBER: 142:463178

TITLE: Highly Enantioselective Phase-Transfer-Catalyzed Alkylation of Protected  $\alpha$ -Amino Acid Amides toward Practical Asymmetric Synthesis of Vicinal Diamines,  $\alpha$ -Amino Ketones, and  $\alpha$ -Amino Alcohols

AUTHOR(S): Ooi, Takashi; Takeuchi, Mifune; Kato, Daisuke; Uematsu, Yukitaka; Tayama, Eiji; Sakai, Daiki; Maruoka, Keiji

CORPORATE SOURCE: Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto, Sakyo, 606-8502, Japan

SOURCE: Journal of the American Chemical Society (2005), 127(14), 5073-5083

CODEN: JACSAT; ISSN: 0002-7863

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 142:463178

AB Highly enantioselective  $\alpha$ -alkylation of protected glycine diphenylmethyl (Dpm) and Weinreb amides  $\text{Ph}_2\text{C:NCH}_2\text{CONR}_1\text{R}_2$  ( $\text{R}_1 = \text{H}$ ,  $\text{R}_2 = \text{Ph}_2\text{CH}$ ;  $\text{R}_1 = \text{Me}$ ,  $\text{PhCH}_2$ ,  $\text{R}_2 = \text{MeO}$ ) has been realized under phase-transfer conditions by the successful utilization of binaphthalene-based designer chiral quaternary ammonium salt as a catalyst. Particularly, remarkable reactivity of the chiral ammonium enolate derived from this catalyst and  $\text{Ph}_2\text{C:NCH}_2\text{CONR}_1\text{R}_2$  ( $\text{R}_1 = \text{H}$ ,  $\text{R}_2 = \text{Ph}_2\text{CH}$ ) allowed the reaction with less reactive simple secondary alkyl halides with high efficiency and enantioselectivity. An addnl. unique feature of this chiral ammonium enolate is its ability to recognize the chirality of  $\beta$ -branched primary alkyl halides, which provides impressive levels of kinetic resolution and double stereodifferentiation during the alkylation, allowing for two  $\alpha$ - and  $\gamma$ -stereocenters to be controlled. Combined with the subsequent reduction using  $\text{LiAlH}_4$  in cyclopentyl Me ether, this system offers a facile access to structurally diverse optically active vicinal diamines. Furthermore, the optically active  $\alpha$ -amino acid Weinreb amides ( $\text{R}$ )- $\text{Ph}_2\text{C:NCHR}_3\text{CONR}_4(\text{OMe})$  ( $\text{R}_3 = \text{Me}$ ,  $\text{PhCH}_2$ ;  $\text{R}_4 = \text{Et}$ ,  $\text{Bu}$ ,  $\text{H}_2\text{C:CHCH}_2$ , 1-naphthylmethyl, etc.) can be efficiently converted to the corresponding amino ketones by a simple treatment with Grignard reagents. In addition, reduction and alkylation of the optically active  $\alpha$ -amino ketone into both syn and anti  $\alpha$ -amino alcs. with almost complete relative and absolute stereochem. control have been achieved. With (S,S)- and (R,R)-binaphthalene-based designer chiral quaternary ammonium salts as catalysts in hand, the present approach renders both enantiomers of  $\alpha$ -amino amides including Weinreb amides readily available with enormous structural variation and also establishes a general and practical route to vicinal diamines,  $\alpha$ -amino ketones, and  $\alpha$ -amino alcs. with the desired stereochem.

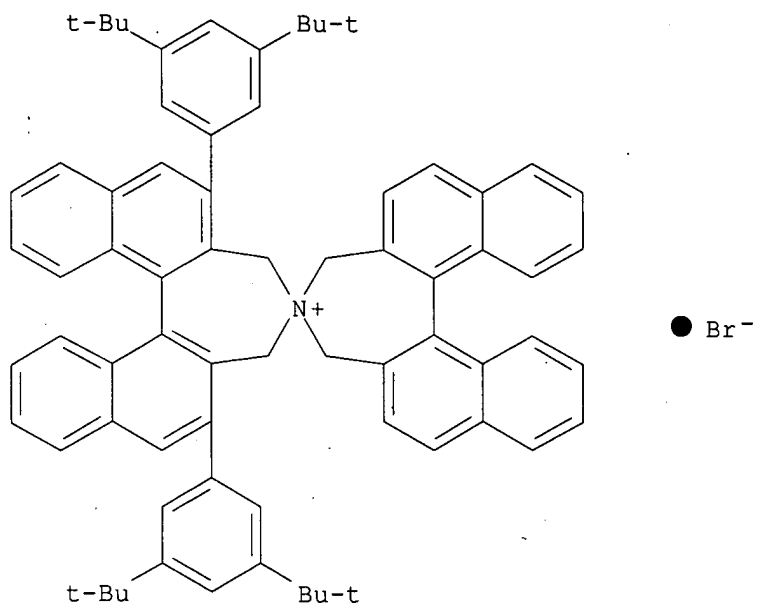
IT 501934-20-9 501934-21-0

RL: CAT (Catalyst use); USES (Uses)

(asym. synthesis of vicinal diamines,  $\alpha$ -amino ketones,  $\alpha$ -amino alcs. and their derivs. via enantioselective phase-transfer alkylation of protected  $\alpha$ -amino acid amides catalyzed by binaphthalene-based quaternary ammonium salts)

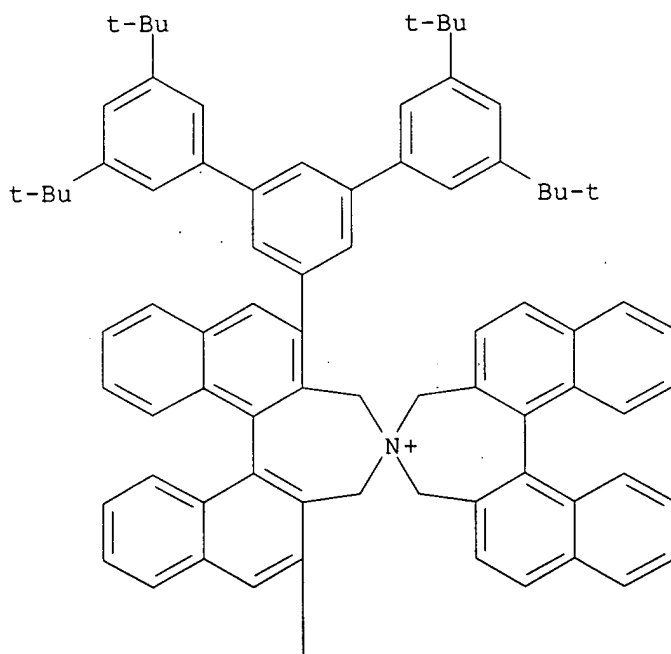
RN 501934-20-9 CAPLUS

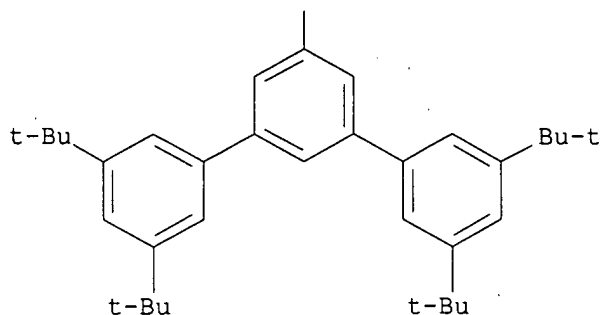
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(1,1-dimethylethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide (1:1), (11bS,11'bS)-(CA INDEX NAME)



RN 501934-21-0 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[3,3'',5,5''-tetrakis(1,1-dimethylethyl)[1,1':3',1''-terphenyl]-5'-yl]-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)

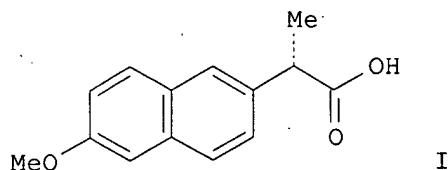
PAGE 1-A





REFERENCE COUNT: 90 THERE ARE 90 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 26 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2005:124720 CAPLUS  
 DOCUMENT NUMBER: 142:355013  
 TITLE: A simple catalytic route to naproxen  
 AUTHOR(S): Kumar, Sanjeev; Ramachandran, Uma  
 CORPORATE SOURCE: Department of Pharmaceutical Technology, National  
 Institute of Pharmaceutical Education & Research  
 (NIPER), Punjab, 160 062, India  
 SOURCE: Tetrahedron: Asymmetry (2005), 16(3), 647-649  
 CODEN: TASYE3; ISSN: 0957-4166  
 PUBLISHER: Elsevier B.V.  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 OTHER SOURCE(S): CASREACT 142:355013  
 GI



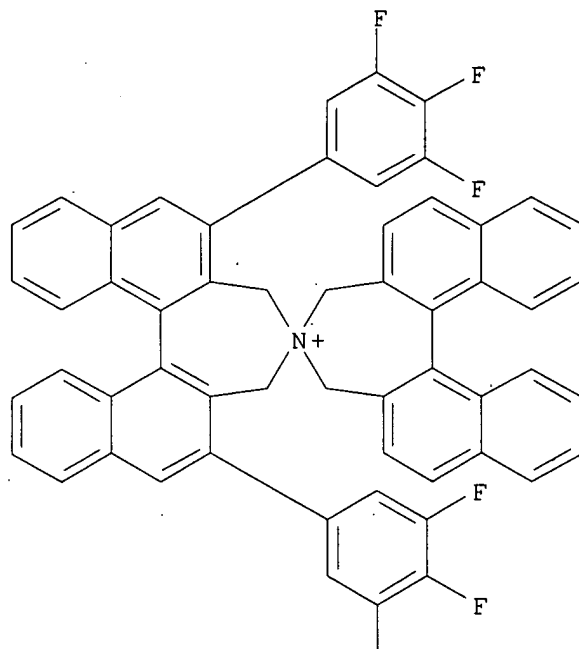
I

AB The asym. synthesis of naproxen (I) involving catalytic enantioselective methylation is reported. The reaction was conducted in a solid-liquid biphasic system using chiral quaternary ammonium salts.

IT 287384-12-7  
 RL: CAT (Catalyst use); USES (Uses)  
 (stereoselective preparation of naproxen via asym. methylation of (methoxynaphthyl)acetate catalyzed by chiral spiro quaternary ammonium salt followed by hydrolysis)

RN 287384-12-7 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'BS)- (CA INDEX NAME)



REFERENCE COUNT: 29 THERE ARE 29 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 27 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2005:87810 CAPLUS  
 DOCUMENT NUMBER: 142:317049  
 TITLE: Dramatic rate enhancement of asymmetric phase-transfer-catalyzed alkylations  
 AUTHOR(S): Shirakawa, Seiji; Yamamoto, Kenichiro; Kitamura, Masanori; Ooi, Takashi; Maruoka, Keiji  
 CORPORATE SOURCE: Department of Chemistry, Kyoto University, Sakyo, Kyoto, 606-8502, Japan  
 SOURCE: Angewandte Chemie, International Edition (2005), 44(4), 625-628  
 CODEN: ACIEF5; ISSN: 1433-7851  
 PUBLISHER: Wiley-VCH Verlag GmbH & Co. KGaA  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 OTHER SOURCE(S): CASREACT 142:317049  
 GI

AB Nonracemic amino acid ester benzophenone imines I (R = Et, H<sub>2</sub>C:CHCH<sub>2</sub>, PhCH<sub>2</sub>, 1-naphthylmethyl) are prepared in 63-98% yields and in 91-98% ee by alkylation of tert-Bu glycinate benzophenone imine I (R = H) with either alkyl bromides RBr or Et iodide and potassium hydroxide in the presence of 0.05-0.5 mol% nonracemic tetraalkylammonium bromide II•Br- and either crown ethers such as 18-crown-6 or tetrabutylammonium or tetraoctylammonium bromides using toluene and water in a biphasic mixture 18-Crown-6, dicyclohexano-18-crown-6, and crypt-2,2,2 are all effective phase transfer catalysts for the enantioselective alkylation, while neither 15-crown-5 or 12-crown-4 are effective catalysts. Tetramethylammonium bromide, N-methylpyridinium iodide and N-butylpyridinium chloride are ineffective ammonium salt phase transfer catalysts for the enantioselective alkylation. 0.05-0.1 Mol% of II•Br- can be used as a catalyst in the presence of 18-crown-6 if reactive alkyl halides are used; alkylation using Et iodide requires 0.5-1.0 mol% of II•Br- and 0.5 mol% of 18-crown-6 to achieve effective alkylation rates.

IT 466679-93-6

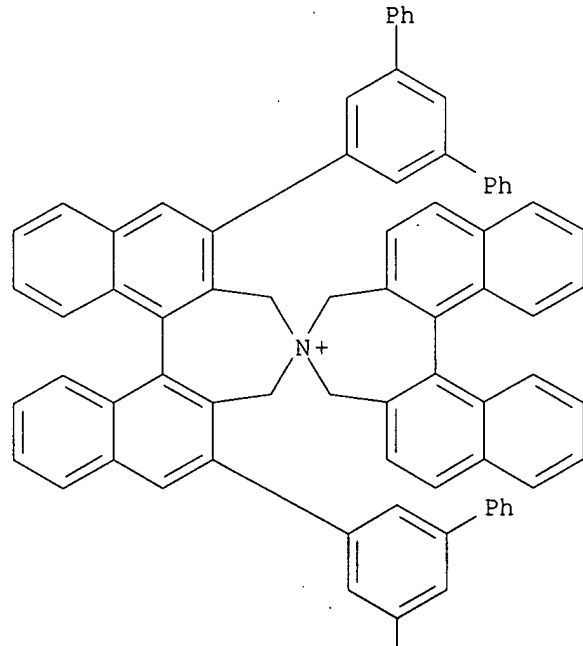
RL: CAT (Catalyst use); USES (Uses)

(enantioselective preparation of amino acid tert-Bu ester benzophenone imines by alkylation of tert-Bu glycinate benzophenone imine in presence of nonracemic phase transfer catalyst and either crown ethers or tetraalkylammonium salts)

RN 466679-93-6 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis([1,1':3',1''-terphenyl]-5'-yl)-3,3',5,5'-tetrahydro-, bromide (1:1), (11bR,11'bR)- (CA INDEX NAME)

PAGE 1-A





Ph

● Br<sup>-</sup>

REFERENCE COUNT: 46 THERE ARE 46 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 28 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2005:71165 CAPLUS

DOCUMENT NUMBER: 142:176719

TITLE: Preparation of optically active spiro-binaphthyl quaternary ammonium salts, process for producing the same, and process for producing optically active  $\alpha$ -amino acid derivative with the same

INVENTOR(S): Maruoka, Keiji

PATENT ASSIGNEE(S): Tosoh Corporation, Japan

SOURCE: PCT Int. Appl., 109 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: Japanese

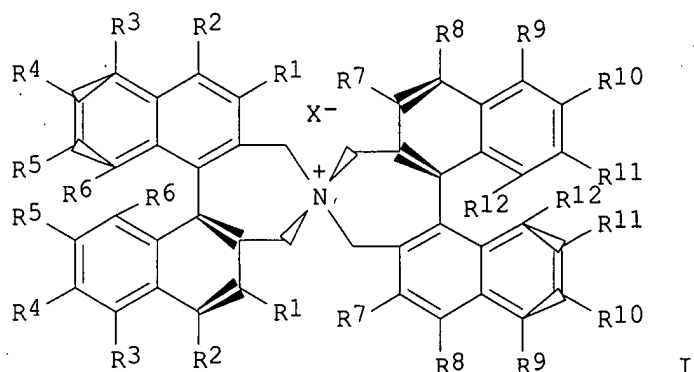
FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005007622	A2	20050127	WO 2004-JP10387	20040722
WO 2005007622	A3	20050331		
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
JP 2005041791	A	20050217	JP 2003-200673	20030723
JP 2005041792	A	20050217	JP 2003-200674	20030723
EP 1650212	A2	20060426	EP 2004-770860	20040722
R: CH, DE, GB, LI				
US 20060183896	A1	20060817	US 2006-563658	20060207
PRIORITY APPLN. INFO.:			JP 2003-200673	A 20030723
			JP 2003-200674	A 20030723
			WO 2004-JP10387	W 20040722

OTHER SOURCE(S): MARPAT 142:176719

GI



AB Optically active quaternary ammonium salts (I) [R1-R12 = H, Me, Et; each C3-18 straight-chain, branched or cyclic alkyl, heteroalkyl, alkenyl, or alkynyl, C1-18 alkoxy, C5-20 aryl, each C5-35 aralkyl or heteroaralkyl; provided that at least one of R1 -R12 is R13R14R15Si; wherein R13-R15 = Me, Et, vinyl, each C3-18 each C3-18 straight-chain, branched or cyclic alkyl, heteroalkyl, alkenyl, or alkynyl, C1-18 alkoxy, C5-20 aryl, each C5-35 aralkyl or heteroaralkyl; X = F, Cl, Br, iodo, p-toluenesulfonyloxy, HO, thiocyanato, HSO4, ClO4, PF6; a combination of axial asymmetry in the two binaphthyl moiety is (R,R) or (S,S)] are prepared When used as an asym.-axis-containing spiro type phase-transfer catalyst for the asym. alkylation of a glycine derivative, these compds. show high stereoselectivity for substrates such as ones having a small mol. size, e.g., Me iodide, and sec-alkyl halides. An optically active  $\alpha$ -amino acid derivative is produced stereoselectively and useful as an intermediate for medicines and agricultural chems. A novel optically active quaternary ammonium salt I has high performance when used as an asym.-axis-containing spiro type phase-transfer catalyst for the asym. alkylation of a glycine derivative, and in which the rings constituting the spiro skeleton have the same structure, which is advantageous from the standpoint of the number of catalyst synthesis steps. An asym.-axis-containing spiro type ammonium salt I having an alkyl- or aryl-substituted silyl group introduced on an aromatic ring is used as a phase-transfer catalyst to conduct the asym. alkylation of a glycine derivative. An asym.-axis-containing spiro type ammonium salt I having introduced therein a substituent including a perfluoroalkyl group is used in the asym. alkylation of a glycine derivative and then recovered with a fluorous solvent. Thus, 3.15 mmol 4,6,4',6'-tris(tributylsilyl)-2,2'-bis(bromomethyl)-1,1'-binaphthyl, 28% aqueous NH3 solution (0.77 mL, 12.6 mmol), and 5 mL MeCN were heated at reflux in a sealed tube with stirring for 24 h to give spiro-binaphthyl ammonium bromide I (R2 = R4 = R8 = R10 = SiBu3, R1 = R3 = R5 = R6 = R7 = R9 = R11 = R12 = H) (II). Benzyl bromide (0.6 mmol) was added dropwise to a mixture of 0.5 mmol N-(diphenylmethylene)glycine tert-Bu ester, 0.05 mmol II, and 1.0 mL 50% aqueous NaOH solution at 0° and the resulting mixture was stirred at 0° 50 h 92% N-(diphenylmethylene)-L-phenylalanine tert-Bu ester (99% ee).

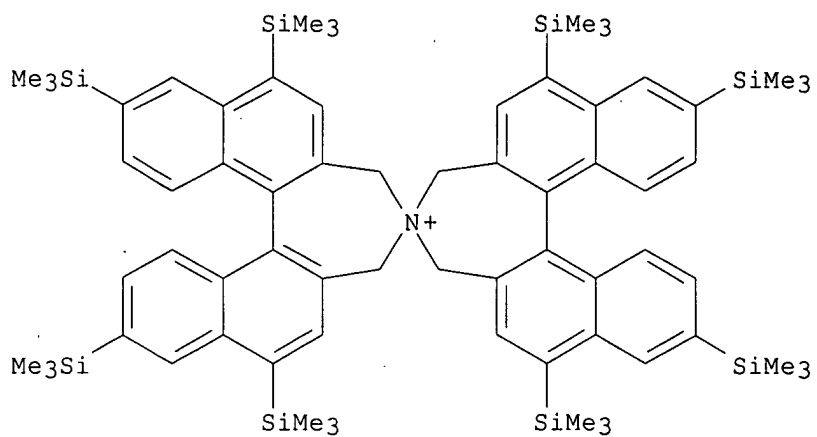
IT 832745-36-5P 832745-37-6P 832745-38-7P  
832745-39-8P 832745-40-1P

RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
USES (Uses)

(preparation of optically active spiro-binaphthyl quaternary ammonium salts as phase-transfer catalysts for preparation of  $\alpha$ -amino acids by asym. alkylation of glycine derivative)

RN 832745-36-5 CAPLUS

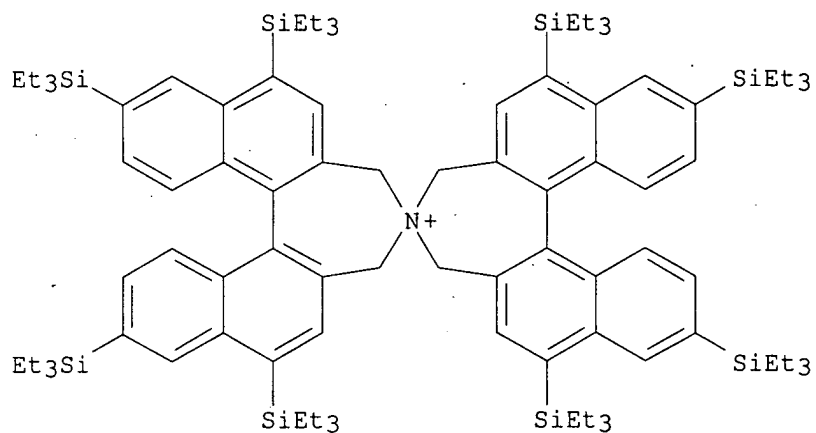
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-1,1',7,7',9,9',14,14'-octakis(trimethylsilyl)-, bromide, (11bR,11'bR)-(9CI) (CA INDEX NAME)



● Br<sup>-</sup>

RN 832745-37-6 CAPLUS

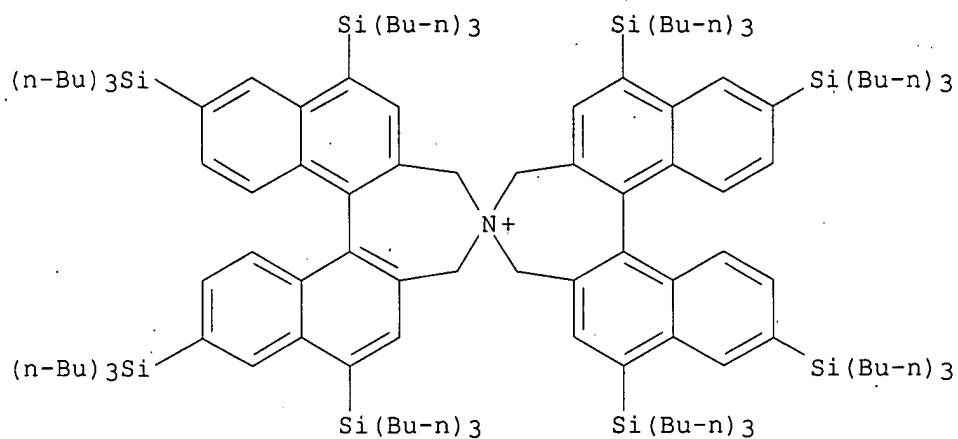
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-1,1',7,7',9,9',14,14'-octakis(trimethylsilyl)-, bromide, (11bR,11'bR)-(9CI) (CA INDEX NAME)



● Br<sup>-</sup>

RN 832745-38-7 CAPLUS

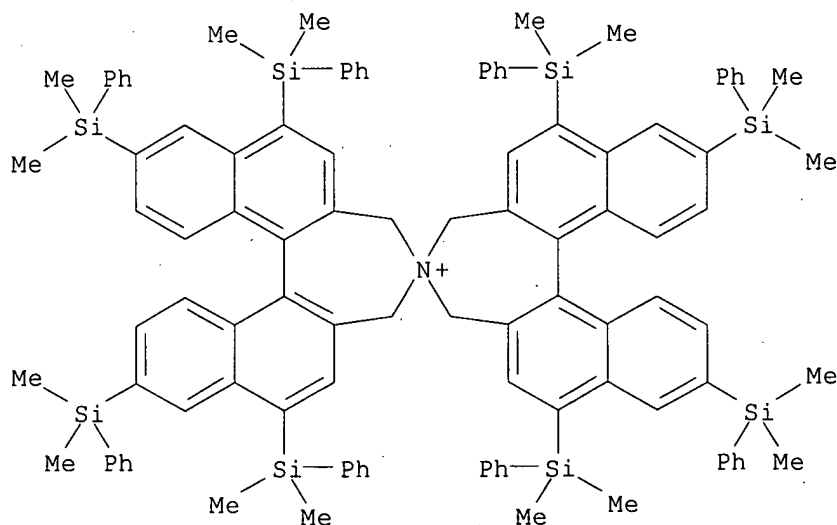
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-1,1',7,7',9,9',14,14'-octakis(tributylsilyl)-, bromide, (11bR,11'bR)-(9CI) (CA INDEX NAME)



● Br<sup>-</sup>

RN 832745-39-8 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 1,1',7,7',9,9',14,14'-  
 octakis(dimethylphenylsilyl)-3,3',5,5'-tetrahydro-, bromide, (11bR,11'bR)-  
 (9CI) (CA INDEX NAME)

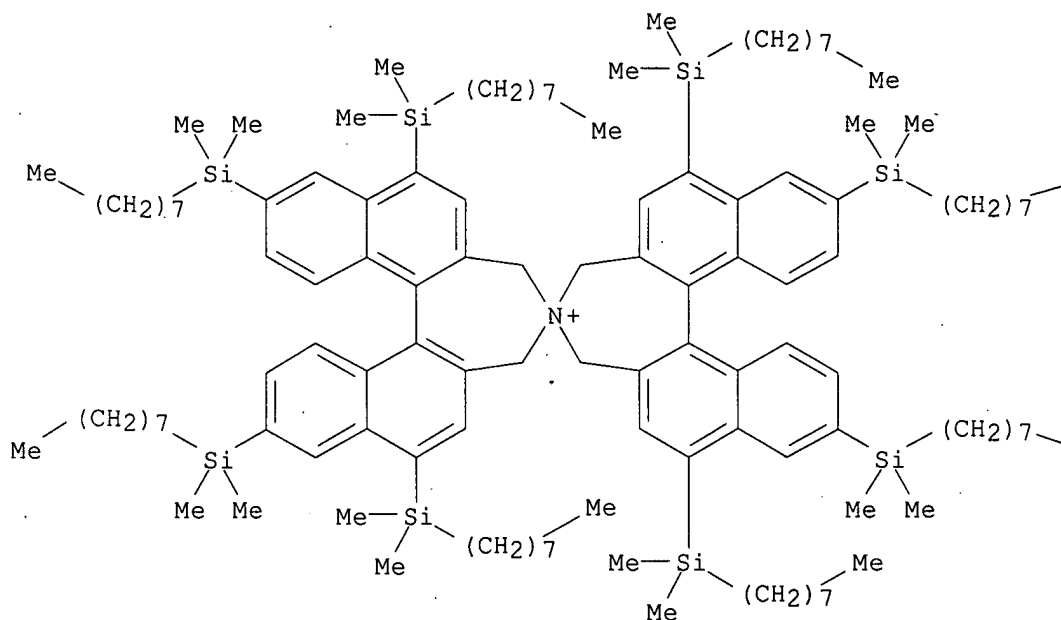
PAGE 1-A



PAGE 2-A

● Br<sup>-</sup>

RN 832745-40-1 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 1,1',7,7',9,9',14,14'-  
 octakis(dimethyloctylsilyl)-3,3',5,5'-tetrahydro-, bromide (1:1),  
 (11bR,11'bR)- (CA INDEX NAME)



Me

● Br<sup>-</sup>

Me

L3 ANSWER 29 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2005:67535 CAPLUS

DOCUMENT NUMBER: 142:298297

TITLE: Highly Enantioselective Phase-Transfer Catalytic Alkylation in the Preparation of Non-natural  $\alpha$ -Amino Acids via Solid Phase Synthesis Using Aldimine Linker

AUTHOR(S): Park, Hyeung-geun; Kim, Mi-Jeong; Park, Mi-Kyung; Jung, Hyun-Ju; Lee, Jihye; Choi, Sea-hoon; Lee, Yeon-Ju; Jeong, Byeong-Seon; Lee, Jeong-Hee; Yoo, Mi-Sook; Ku, Jin-Mo; Jew, Sang-sup

CORPORATE SOURCE: Research Institute of Pharmaceutical Science and College of Pharmacy, Seoul National University, Seoul, 151-742, S. Korea

SOURCE: Journal of Organic Chemistry (2005), 70(5), 1904-1906

PUBLISHER: CODEN: JOCEAH; ISSN: 0022-3263  
 DOCUMENT TYPE: American Chemical Society  
 LANGUAGE: Journal  
 OTHER SOURCE(S): English  
 CASREACT 142:298297.

AB A new Merrifield resin-bound glycinimine tert-Bu ester was prepared and applied to the enantioselective synthesis of non-natural  $\alpha$ -amino acids. For example, Merrifield resin-supported glycinimine tert-Bu ester was alkylated with RBr (R = n-hexyl, allyl, methylallyl, propargyl, benzyl, 4-fluorobenzyl, 4-cyanobenzyl, 4-methylbenzyl, 4-tert-butylbenzyl, 2-naphthylmethyl, 9-anthracenylmethyl) in the presence of 10 mol % of phase transfer catalyst, N-(9-anthracenylmethyl)-O(9)-allylcinchonidium bromide, in aqueous CsOH in toluene/chloroform (7:3) at 0°. Following resin cleavage, and N-benzoylation, protected amino acids PhCONHCH(R)CO<sub>2</sub>Bu-t were obtained with high enantioselectivities (86 to >99% enantiomeric excess).

IT 287384-12-7

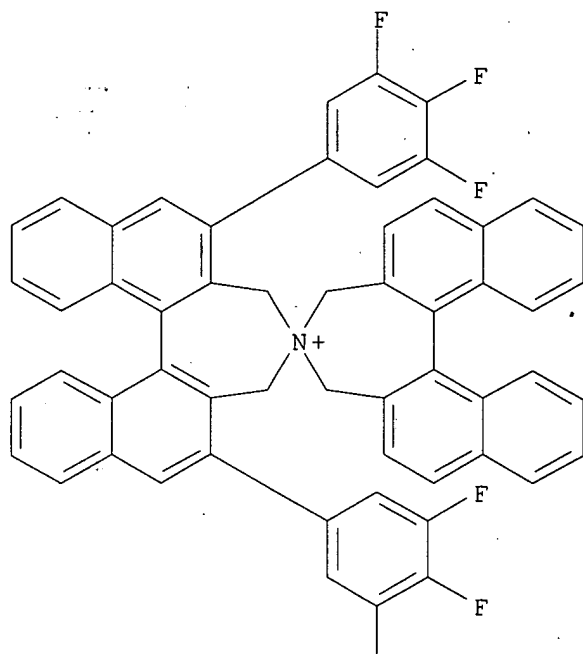
RL: CAT (Catalyst use); USES (Uses)

(preparation of amino acids via asym. alkylation of Merrifield resin-bound glycinimine tert-Bu ester by alkyl/aryl bromides in presence of a phase transfer catalyst)

RN 287384-12-7 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)

PAGE 1-A



PAGE 2-A

F

● Br<sup>-</sup>

ACCESSION NUMBER: 2004:1076624 CAPLUS  
 DOCUMENT NUMBER: 142:38019  
 TITLE: Preparation of  $\gamma$ -nitro carbonyl compounds  
 INVENTOR(S): Maruoka, Keiji; Oi, Takashi  
 PATENT ASSIGNEE(S): Nagase & Co., Ltd., Japan  
 SOURCE: Jpn. Kokai Tokkyo Koho, 61 pp.  
 CODEN: JKXXAF  
 DOCUMENT TYPE: Patent  
 LANGUAGE: Japanese  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 2004352708	A	20041216	JP 2004-89863	20040325
PRIORITY APPLN. INFO.:			JP 2003-127516	A 20030502
OTHER SOURCE(S):	MARPAT 142:38019			
GI				

\* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT \*

AB Title compds. are prepared by reaction of  $R_1CH:N+(O-)OSiR_2R_3R_4$  (I;  $R_1 = C_1-6$  alkoxy, (un)substituted  $C_1-5$  alkyl;  $R_2-R_4 = C_1-5$  alkyl) with  $R_7CH:CR_8COR_8'$  [ $R_7 = C_1-8$  (halo)alkyl,  $C_2-8$  (halo)alkenyl,  $C_2-8$  (halo)alkynyl, (un)substituted (hetero)aralkyl, etc.;  $R_8, R_8' = H, C_1-8$  (halo)alkyl,  $C_2-8$  (halo)alkenyl,  $C_2-8$  (halo)alkynyl, (un)substituted (hetero)aralkyl, etc.] in the presence of optically active quaternary ammonium bifluorides II [ $R_5, R_6 = H, C_1-8$  (halo)alkyl,  $C_2-8$  (halo)alkenyl,  $C_2-8$  (halo)alkynyl, (un)substituted (hetero)aralkyl, etc.;  $Y, Z = H, \text{organic group}$ ] and desilylation of optically active enol silyl ethers. Trans-cinnamaldehyde was treated with I ( $R_1-R_4 = Me$ ) in THF in the presence of quaternary ammonium III [ $Ar_1 = 3,5\text{-bis(trifluoromethyl)phenyl}$ ] at  $-78^\circ$  for 0.5 h and treated with HCl at  $0^\circ$  to give 68% 4-nitro-3-phenylpentanol (anti/syn = 85/15).

IT 586344-86-7P 807619-16-5P

RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
 USES (Uses)

(preparation of  $\gamma$ -nitro carbonyl compds. via addition of silyl nitronates to unsatd. carbonyl compds. using chiral ammonium catalysts)

RN 586344-86-7 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
 2,6-bis[3,3'',5,5''-tetrakis(trifluoromethyl)[1,1':3',1''-terphenyl]-5'-yl]-, (11bR,11'bR)-, (hydrogen difluoride) (1:1) (CA INDEX NAME)

CM 1

CRN 586344-85-6

CMF C88 H48 F24 N

REFERENCE COUNT: 40 THERE ARE 40 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 30 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2004:1153357 CAPLUS

DOCUMENT NUMBER: 142:261750

TITLE: Asymmetric Synthesis of Functionalized Aza-Cyclic Amino Acids with Quaternary Stereocenters by a Phase-Transfer-Catalyzed Alkylation Strategy

AUTHOR(S): Ooi, Takashi; Miki, Takashi; Maruoka, Keiji  
CORPORATE SOURCE: Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto, 606-8502, Japan

SOURCE: Organic Letters (2005), 7(2), 191-193

CODEN: ORLEF7; ISSN: 1523-7060

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 142:261750

AB Practical asym. synthesis of functionalized aza-cyclic  $\alpha$ -amino acid derivs. possessing quaternary stereocenters has been achieved by the phase-transfer catalyzed alkylation of N-(tert-butoxycarbonyl)-3-oxoproline tert-Bu ester and N-(tert-butoxycarbonyl)-3-oxopipercolic acid tert-Bu ester using a chiral quaternary ammonium bromide as catalyst. Subsequent reduction and alkylation of the 3-keto carbonyl moiety proceeded with complete diastereochem. control to afford the corresponding  $\beta$ -hydroxy aza-cyclic  $\alpha$ -amino acid derivs. having stereochem. defined consecutive quaternary carbon centers.

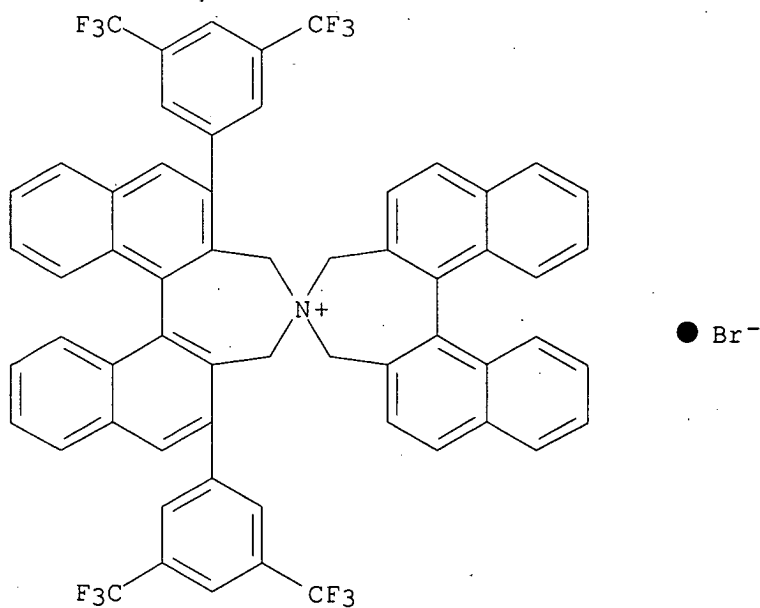
IT 438002-03-0

RL: CAT (Catalyst use); USES (Uses)

(asym. synthesis of functionalized aza-cyclic amino acids with quaternary stereocenters by phase-transfer catalyzed alkylation)

RN 438002-03-0 CAPLUS

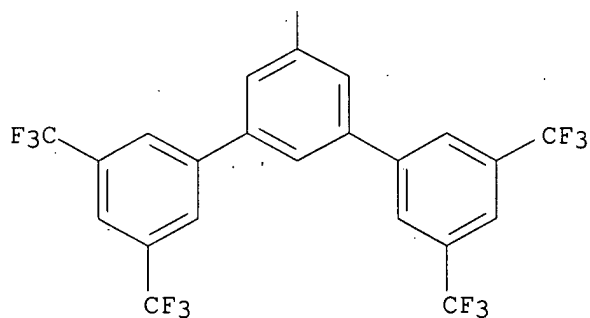
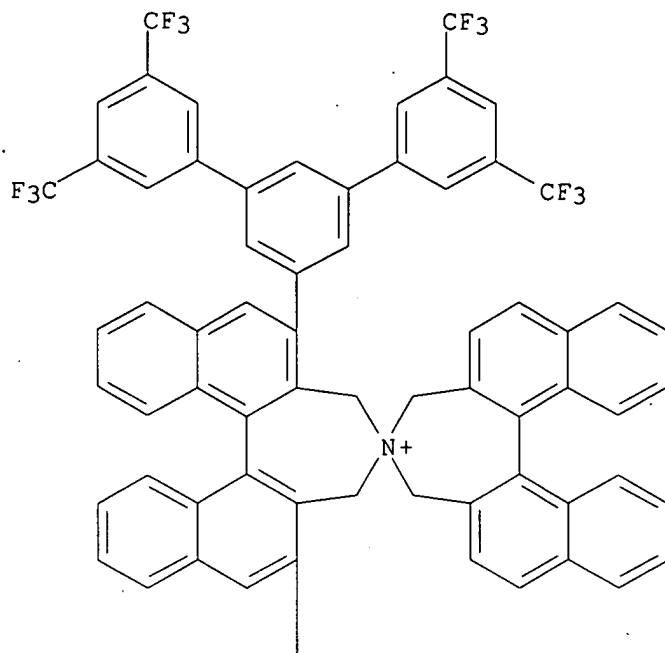
CN 8,8'-Spirobi[8H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



REFERENCE COUNT: 29 THERE ARE 29 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 31 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

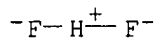




CM 2

CRN 18130-74-0

CMF F2 H



RN 807619-16-5 CAPLUS

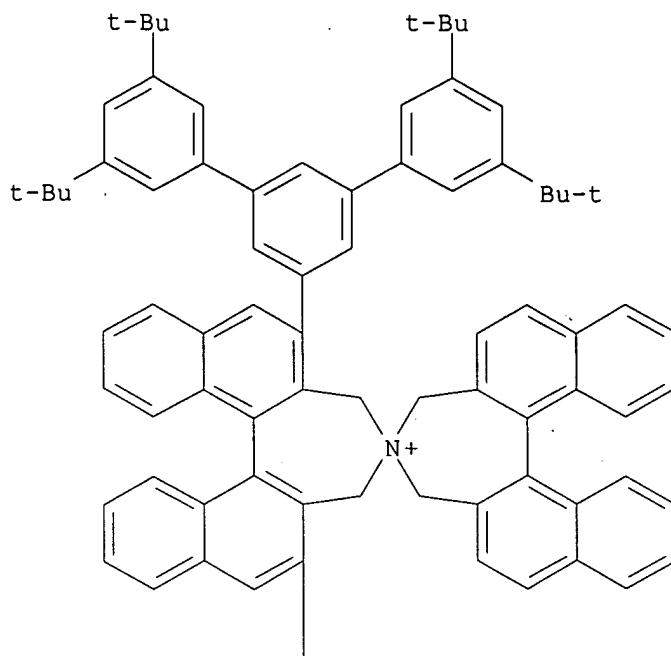
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[3,3'',5,5''-tetrakis(1,1-dimethylethyl)[1,1':3',1''-terphenyl]-5'-yl]-, (11bR,11'bR)-, (hydrogen difluoride) (9CI) (CA INDEX NAME)

CM 1

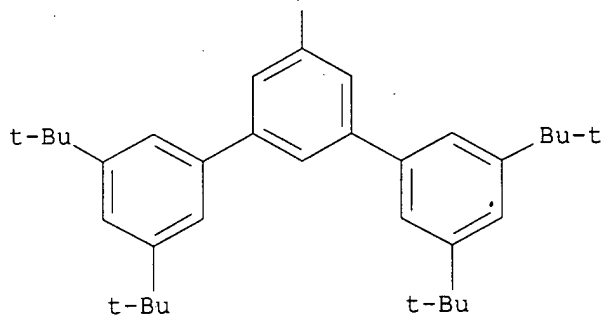
CRN 755750-10-8

CMF C112 H120 N

PAGE 1-A



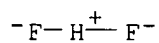
PAGE 2-A



CM 2

CRN 18130-74-0

CMF F2 H



IT 534576-68-6

RL: RCT (Reactant); RACT (Reactant or reagent)

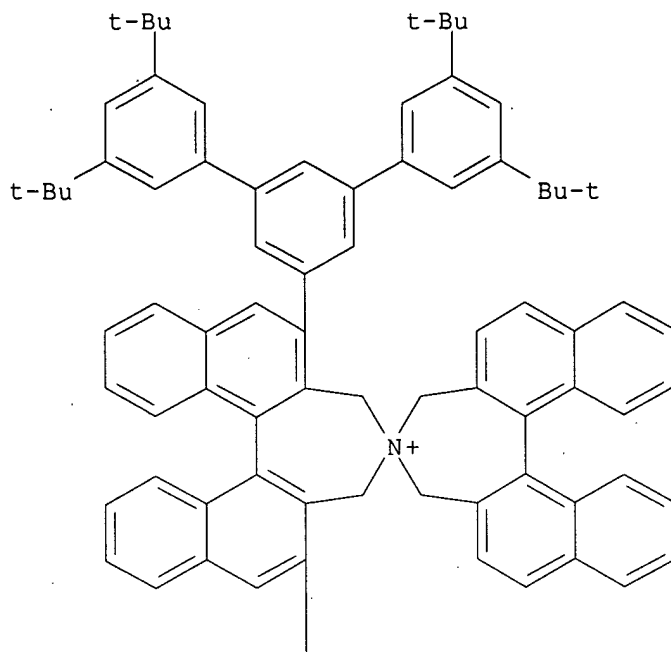
(preparation of  $\gamma$ -nitro carbonyl compds. via addition of silyl nitronates to unsatd. carbonyl compds. using chiral ammonium catalysts)

RN 534576-68-6 CAPLUS

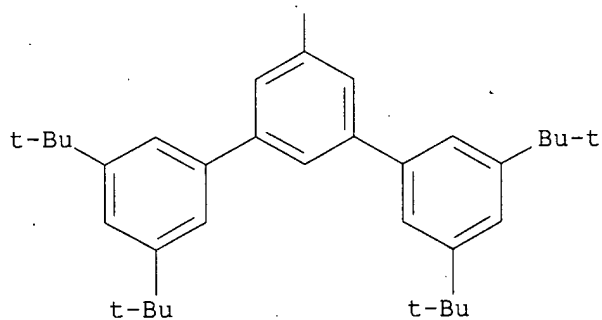
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[3,3'',5,5''-tetrakis(1,1-dimethylethyl)[1,1':3',1''-terphenyl]-5'-

yl]-, bromide, (11bR,11'bR)- (9CI) (CA INDEX NAME)

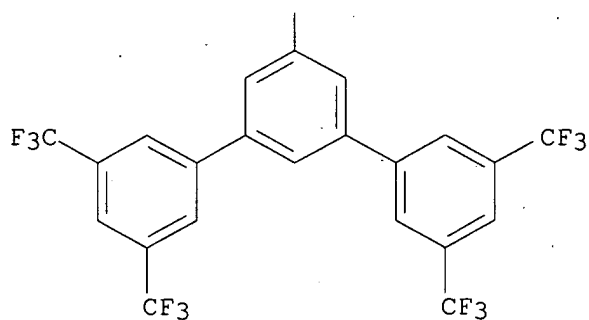
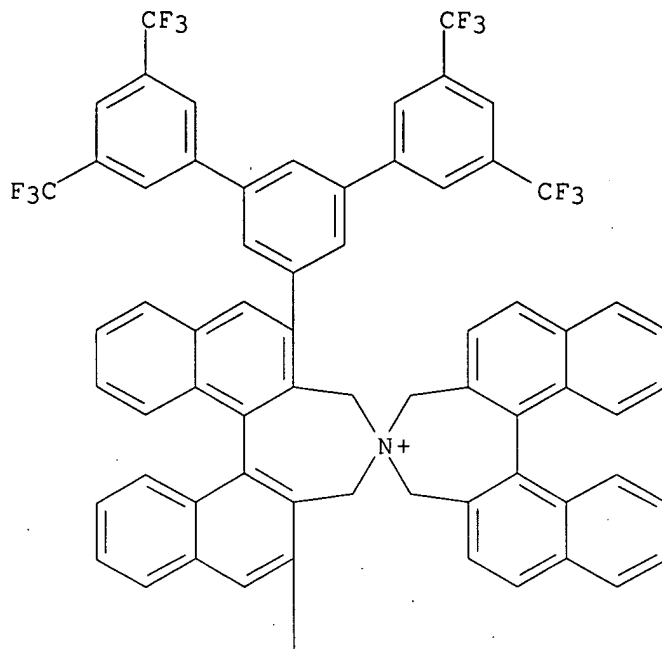
PAGE 1-A



PAGE 2-A



IT 515137-98-1P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT  
 (Reactant or reagent)  
 (preparation of  $\gamma$ -nitro carbonyl compds. via addition of silyl nitronates  
 to unsatd. carbonyl compds. using chiral ammonium catalysts)  
 RN 515137-98-1 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
 2,6-bis[3,3'',5,5''-tetrakis(trifluoromethyl)[1,1':3',1''-terphenyl]-5'-  
 yl]-, bromide, (11bR,11'bR)- (9CI) (CA INDEX NAME)



L3 ANSWER 32 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2004:1068154 CAPLUS  
 DOCUMENT NUMBER: 142:155786  
 TITLE: Studies directed towards asymmetric synthesis of levobupivacaine  
 AUTHOR(S): Kumar, Sanjeev; Ramachandran, Uma  
 CORPORATE SOURCE: Department of Pharmaceutical Technology, National Institute of Pharmaceutical Education & Research (NIPER), Punjab, 160 062, India  
 SOURCE: Tetrahedron Letters (2004), Volume Date 2005, 46(1), 19-21  
 CODEN: TELEAY; ISSN: 0040-4039  
 PUBLISHER: Elsevier B.V.  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English

OTHER SOURCE(S): CASREACT 142:155786

AB The authors report herein the first catalytic asym. synthesis of levobupivacaine. The key step involves the asym. alkylation of N-benzylimine glycineamide.

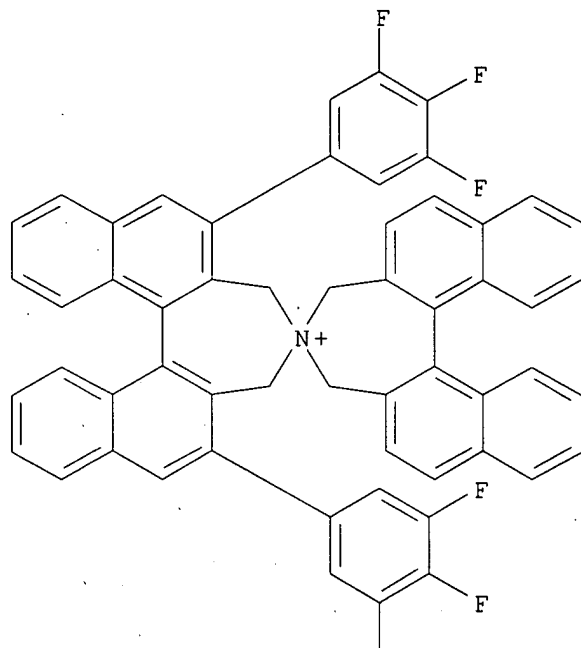
IT 534570-50-8

RL: CAT (Catalyst use); USES (Uses)  
(asym. synthesis of levobupivacaine)

RN 534570-50-8 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bR,11'bR)- (CA INDEX NAME)

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F

● Br<sup>-</sup>

REFERENCE COUNT: 14 THERE ARE 14 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

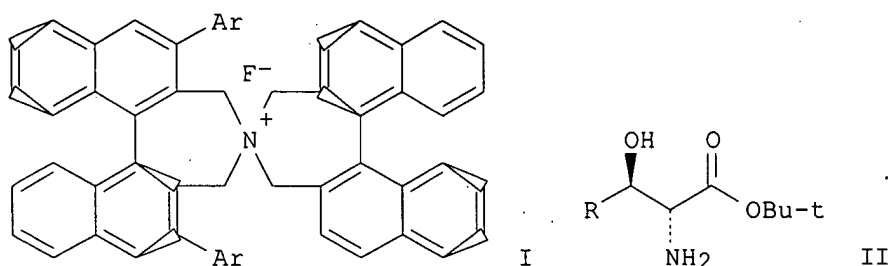
L3 ANSWER 33 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2004:829203 CAPLUS

DOCUMENT NUMBER: 143:44038

TITLE: Anti-selective asymmetric synthesis of  
β-hydroxy-α-amino acid esters by the in  
situ generated chiral quaternary ammonium  
fluoride-catalyzed Mukaiyama-type aldol reaction  
AUTHOR(S): Ooi, Takashi; Taniguchi, Mika; Doda, Kanae; Maruoka,  
Keiji

CORPORATE SOURCE: Department of Chemistry, Graduate School of Science,  
Kyoto University, Kyoto, 606-8502, Japan  
SOURCE: Advanced Synthesis & Catalysis (2004), 346(9 + 10),  
1073-1076  
CODEN: ASCAF7; ISSN: 1615-4150  
PUBLISHER: Wiley-VCH Verlag GmbH & Co. KGaA  
DOCUMENT TYPE: Journal  
LANGUAGE: English  
OTHER SOURCE(S): CASREACT 143:44038  
GI



AB The aldol coupling of RCHO [R = CH<sub>2</sub>CH<sub>2</sub>Ph, (CH<sub>2</sub>)<sub>4</sub>Me, (CH<sub>2</sub>)<sub>5</sub>Me, Bu-i, Pr-i] with (4-FC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C:NCH:C(OSiMe<sub>3</sub>)OBu-t, derived from the glycinate Schiff base, was efficiently catalyzed by an in-situ generated, chiral quaternary ammonium fluoride salt I [Ar = 3,4,5-trifluorophenyl, 3,5-bis(3,5-bis(trifluoromethyl)phenyl)phenyl] under mild, neutral conditions to afford anti-β-hydroxy-α-amino esters II in yields ≥ 58% and enantiomeric excess ≥ 82%.

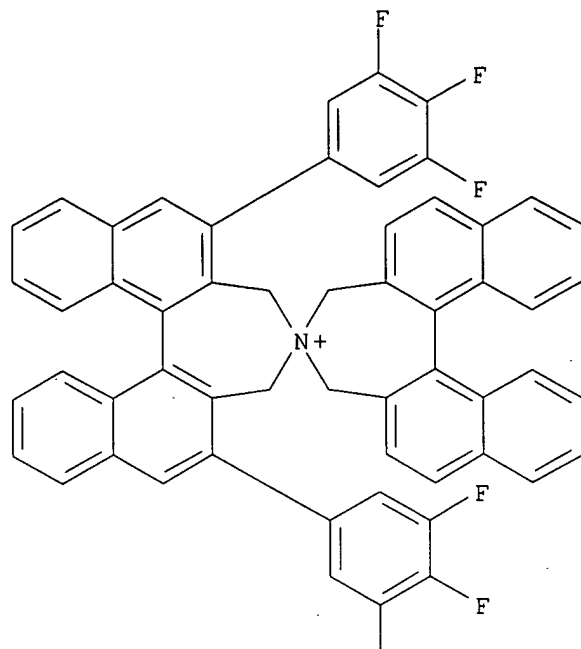
IT 401846-46-6 853642-72-5  
RL: CAT (Catalyst use); RCT (Reactant); RACT (Reactant or reagent); USES (Uses)  
(asym. preparation of anti-hydroxy amino esters via Mukaiyama-type aldol reaction with in-situ generated chiral quaternary ammonium fluoride catalysts)

RN 401846-46-6 CAPLUS  
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, stereoisomer, sulfate (1:1) (9CI) (CA INDEX NAME)

CM 1

CRN 401846-45-5  
CMF C56 H34 F6 N

PAGE 1-A



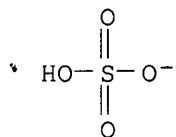
PAGE 2-A



CM 2

CRN 14996-02-2

CMF H O4 S



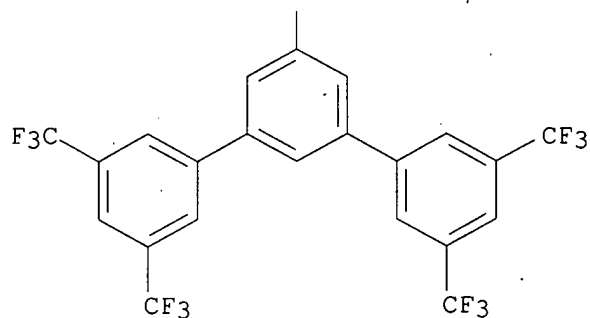
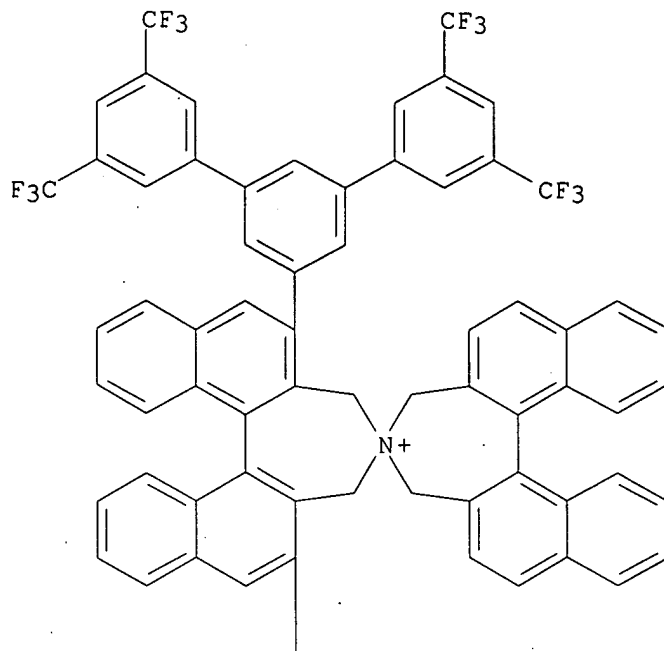
RN 853642-72-5 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[3,3'',5,5''-tetrakis(trifluoromethyl)[1,1':3',1''-terphenyl]-5'-yl]-, (11bS,11'bS)-, sulfate (1:1) (9CI) (CA INDEX NAME)

CM 1

CRN 503538-64-5

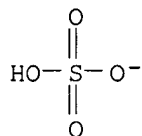
CMF C88 H48 F24 N



CM 2

CRN 14996-02-2

CMF H O4 S



IT 853642-73-6P 853642-74-7P

RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);

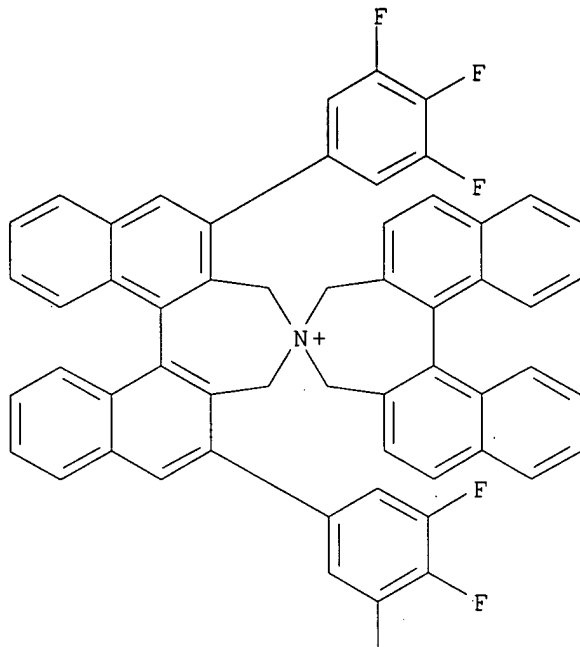
USES (Uses)

(asym. preparation of anti-hydroxy amino esters via Mukaiyama-type aldol reaction with in-situ generated chiral quaternary ammonium fluoride catalysts)



RN 853642-73-6 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
 2,6-bis(3,4,5-trifluorophenyl)-, fluoride, (11bS,11'bs)- (9CI) (CA INDEX  
 NAME)

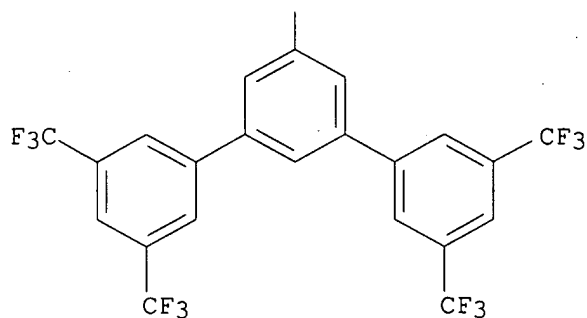
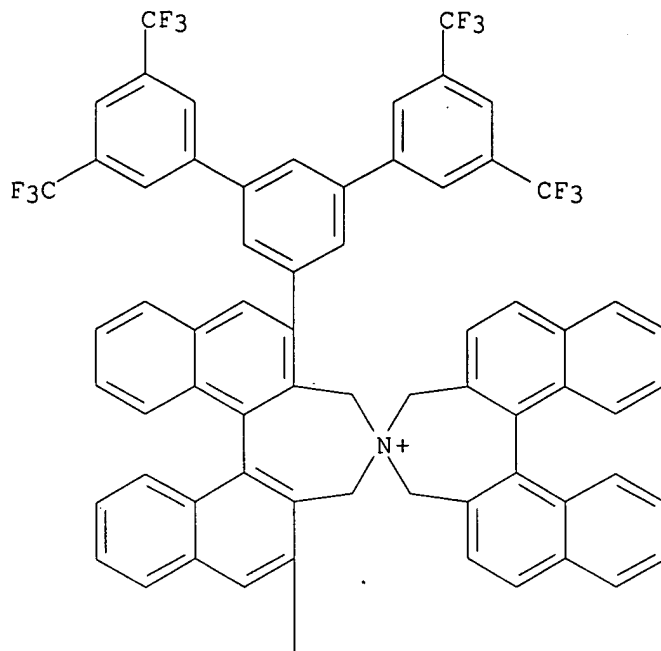
PAGE 1-A



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RN 853642-74-7 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
 2,6-bis[3,3'',5,5''-tetrakis(trifluoromethyl)[1,1':3',1''-terphenyl]-5'-  
 yl]-, fluoride, (11bS,11'bs)- (9CI) (CA INDEX NAME)



● F<sup>-</sup>

REFERENCE COUNT: 47 THERE ARE 47 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 34 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2004:740332 CAPLUS  
 DOCUMENT NUMBER: 141:260392  
 TITLE: Quaternary ammonium bifluoride compound and process for producing chiral nitroalcohol  
 INVENTOR(S): Maruoka, Keiji; Ooi, Takashi  
 PATENT ASSIGNEE(S): Nagase & Co., Ltd., Japan  
 SOURCE: PCT Int. Appl., 60 pp.  
 CODEN: PIXXD2  
 DOCUMENT TYPE: Patent  
 LANGUAGE: Japanese  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2004076459	A1	20040910	WO 2003-JP9500	20030725
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
AU 2003252268	A1	20040917	AU 2003-252268	20030725
PRIORITY APPLN. INFO.:			JP 2003-51773	A 20030227
			WO 2003-JP9500	W 20030725
OTHER SOURCE(S):		MARPAT 141:260392		
GI				

\* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT \*

AB Title compds. I·HF2- [R1, R2 = H, (un)substituted alkyl with halo, etc.] were prepared. Compds. I·HF2- catalyzed process for the preparation of chiral nitroalcs. was provided. For example, to a solution of benzaldehyde (31.8 mg), compound (S,S)-I·HF2- [R1 = R2 = 3,5-bis(3,5-di(CF3)phenyl)phenyl] (9.6 mg) in THF (3 mL) was added trimethylsilylnitronate II (52.9 mg), e.g., prepared from nitroethane, at -98 °C. The resulting solution was stirred at -78 °C for 4 h, followed by aqueous work-up and silica-gel purification afforded (1R,2S)-2-nitro-1-phenylpropan-1-ol in 92% yield, 95% ee.

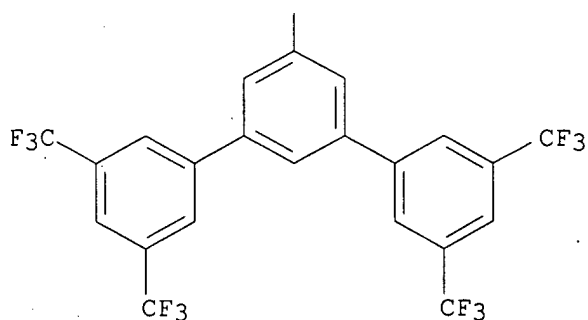
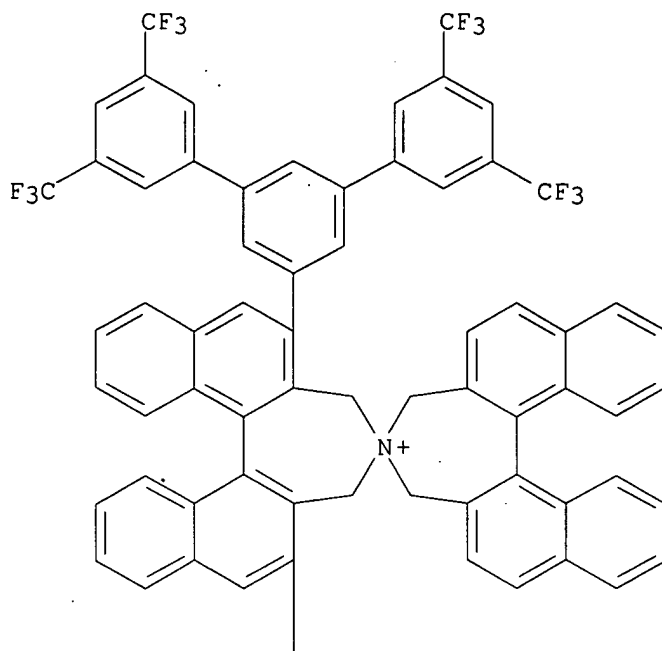
IT 586344-86-7 586344-89-0 756494-03-8  
 756494-05-0  
 RL: CAT (Catalyst use); USES (Uses)  
 (preparation of quaternary ammonium bifluoride catalyst)

RN 586344-86-7 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[3,3'',5,5''-tetrakis(trifluoromethyl)[1,1':3',1''-terphenyl]-5'-yl]-, (11bR,11'bR)-, (hydrogen difluoride) (1:1) (CA INDEX NAME)

CM 1

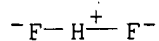
CRN 586344-85-6  
 CMF C88 H48 F24 N



CM 2

CRN 18130-74-0

CMF F2 H



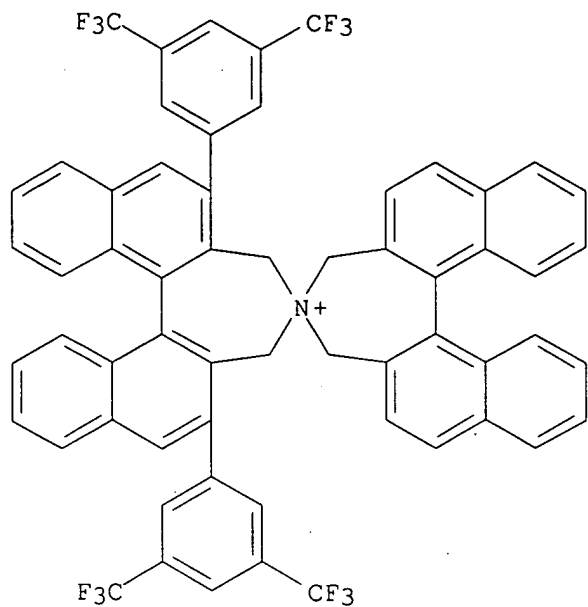
RN 586344-89-0 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, (11bR,11'bR)-, (hydrogen difluoride) (1:1) (CA INDEX NAME)

CM 1

CRN 586344-88-9

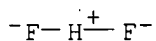
CMF C60 H36 F12 N



CM 2

CRN 18130-74-0

CMF F2 H



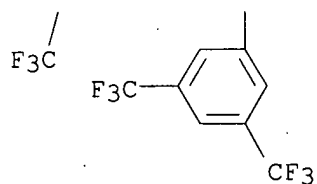
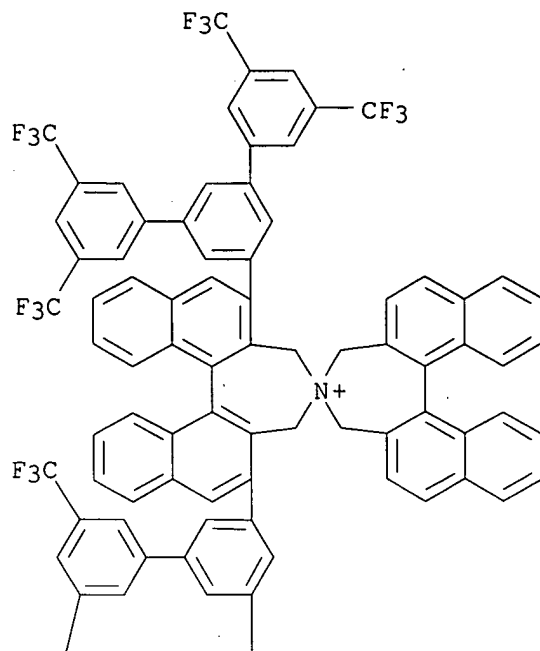
RN 756494-03-8 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[3,3'',5,5''-tetrakis(trifluoromethyl)[1,1':3',1''-terphenyl]-5'-yl]-, (hydrogen difluoride) (9CI) (CA INDEX NAME)

CM 1

CRN 756494-02-7

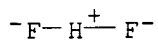
CMF C88 H48 F24 N



CM 2

CRN 18130-74-0

CMF F2 H



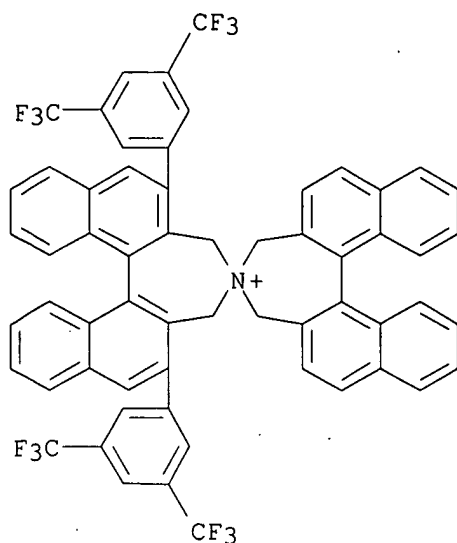
RN 756494-05-0 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, (hydrogen difluoride) (9CI) (CA INDEX NAME)

CM 1

CRN 756494-04-9

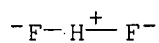
CMF C60 H36 F12 N



CM 2

CRN 18130-74-0

CMF F2 H



IT 503538-63-4P 503538-65-6P

RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);

USES (Uses)

(preparation of quaternary ammonium bifluoride catalyst)

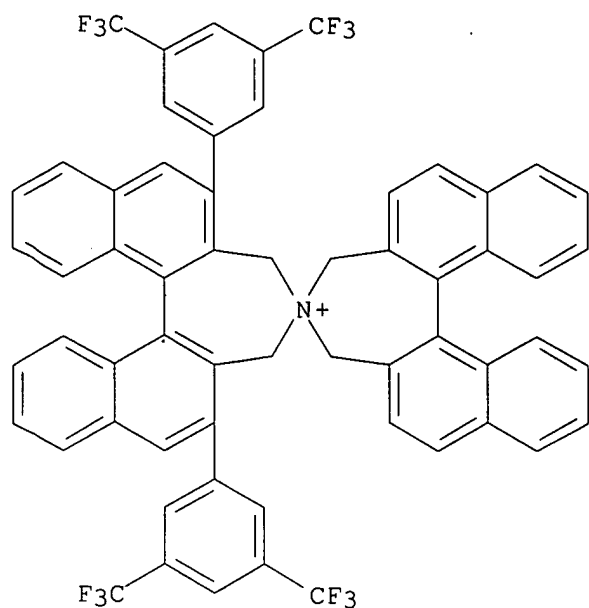
RN 503538-63-4 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, (11bS,11'bs)-, (hydrogen difluoride) (9CI) (CA INDEX NAME)

CM 1

CRN 344550-35-2

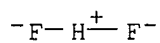
CMF C60 H36 F12 N



CM 2

CRN 18130-74-0

CMF F2 H



RN 503538-65-6 CAPLUS

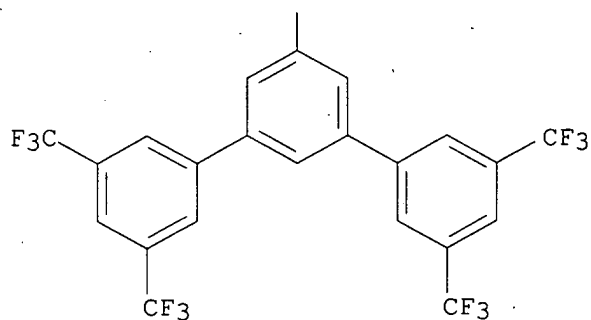
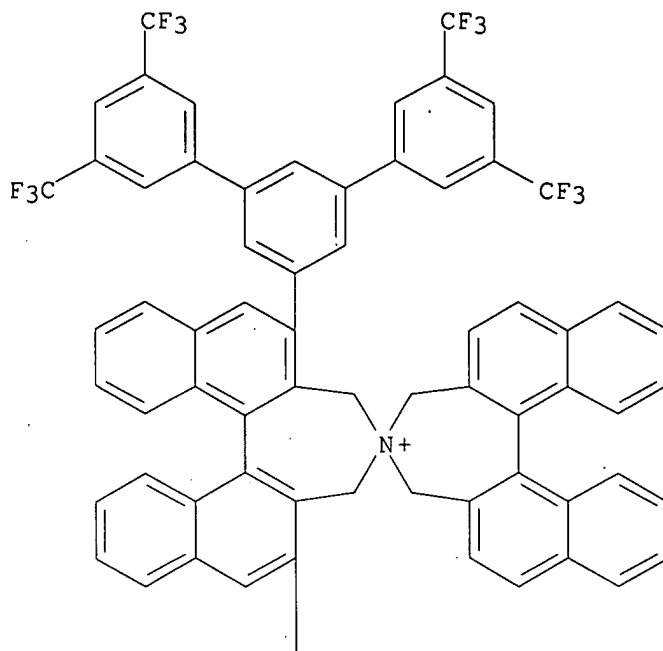
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[3,3'',5,5''-tetraakis(trifluoromethyl)[1,1':3',1''-terphenyl]-5'-yl]-, (11bS,11'bS)-, (hydrogen difluoride) (9CI) (CA INDEX NAME)

CM 1

CRN 503538-64-5

CMF C88 H48 F24 N

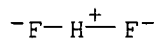




CM 2

CRN 18130-74-0

CMF F2 H



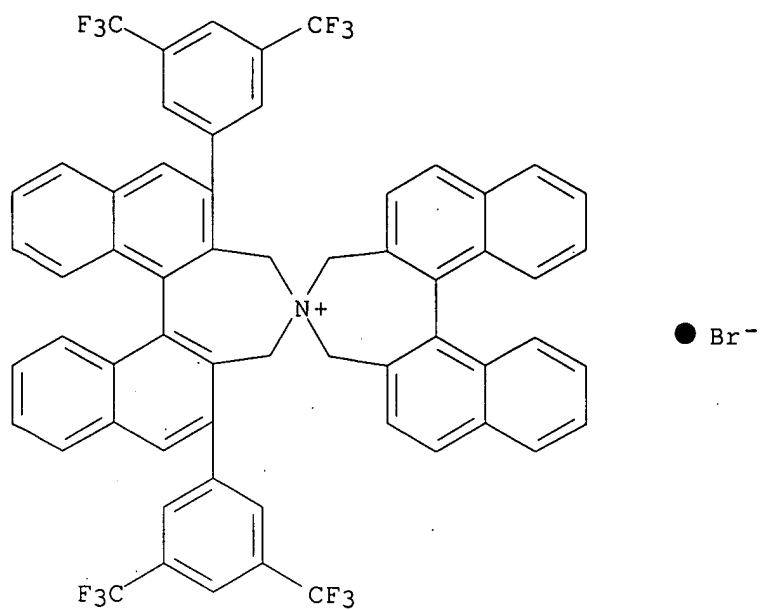
IT 438002-03-0P 503538-60-1P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation of quaternary ammonium bifluoride catalyst)

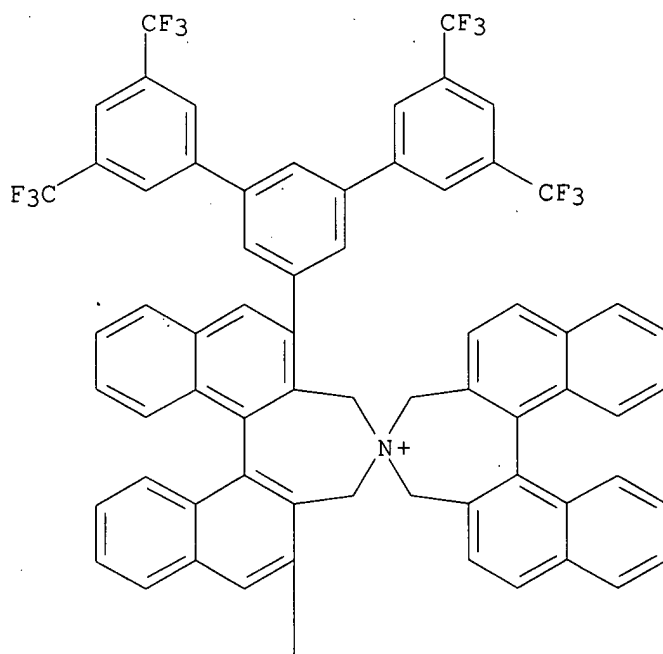
RN 438002-03-0 CAPLUS

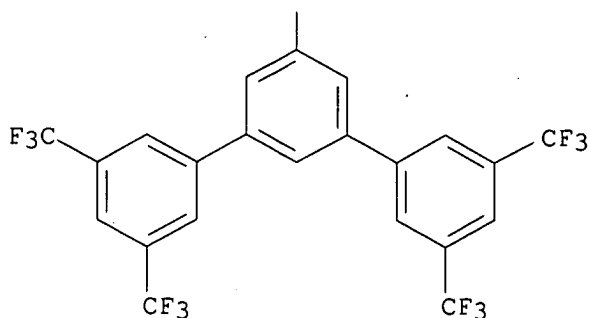
CN 8,8'-Spiro[8H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide (1:1), (11bS,11'bs)- (CA INDEX NAME)



RN 503538-60-1 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[3,3'',5,5''-tetrakis(trifluoromethyl)[1,1':3',1''-terphenyl]-5'-yl]-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)

PAGE 1-A





● Br<sup>-</sup>

REFERENCE COUNT: 1 THERE ARE 1 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 35 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2004:711181 CAPLUS

DOCUMENT NUMBER: 141:379682

TITLE: Highly Enantioselective Conjugate Addition of Nitroalkanes to Alkylidenemalonates Using Efficient Phase-Transfer Catalysis of N-Spiro Chiral Ammonium Bromides

AUTHOR(S): Ooi, Takashi; Fujioka, Shingo; Maruoka, Keiji  
CORPORATE SOURCE: Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto, 606-8502, Japan

SOURCE: Journal of the American Chemical Society (2004), 126(38), 11790-11791

CODEN: JACSAT; ISSN: 0002-7863

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 141:379682

AB Highly enantioselective conjugate addition of nitroalkanes to alkylidenemalonates has been accomplished by using a C2-sym. chiral quaternary ammonium bromide as phase-transfer catalyst. For instance, simple mixing of nitropropane, diisopropyl benzylidenemalonate, Cs2CO3 (1 equiv), and catalyst (1 mol %) in toluene at 0 °C for 2.5 h gave anti-O2NCHEtCHPhCH(CO2Et)2 quant. with 97% ee. The applicability of this procedure has been demonstrated with other representative alkylidenemalonates and nitroalkanes. Since the products can be readily transformed into  $\gamma$ -amino acid hydrochlorides without loss of diastereo- and enantioselectivity, the present method provides a new and practical access to various optically active  $\gamma$ -amino acid derivs.

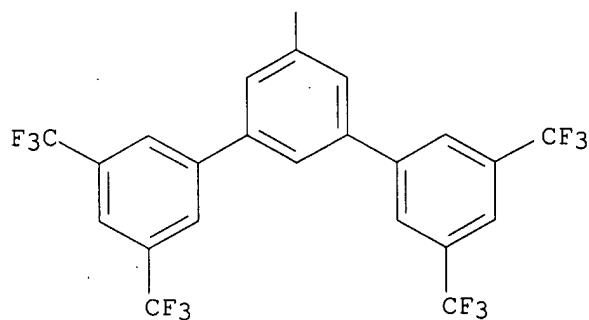
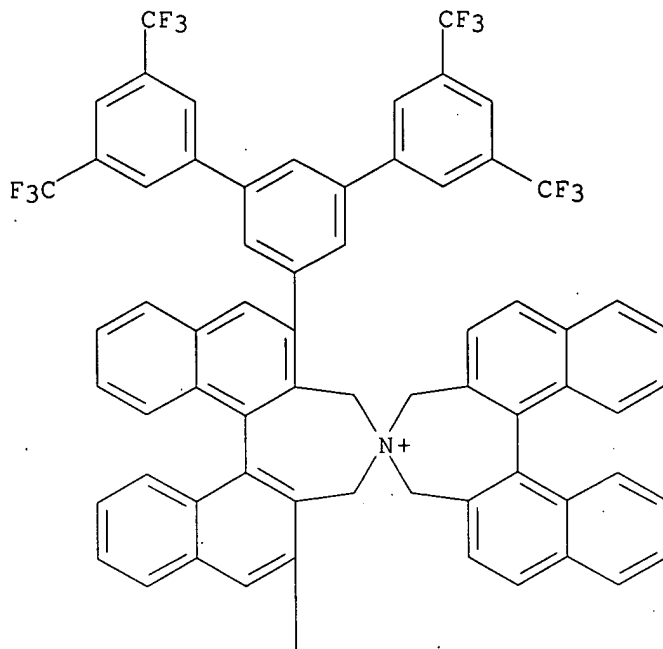
IT 503538-60-1.

RL: CAT (Catalyst use); USES (Uses)

(enantioselective conjugate addition of nitroalkanes to alkylidenemalonates using a C2-sym. chiral quaternary ammonium bromide as phase-transfer catalyst)

RN 503538-60-1 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[3,3'',5,5''-tetrakis(trifluoromethyl)[1,1':3',1''-terphenyl]-5'-yl]-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



● Br<sup>-</sup>

REFERENCE COUNT: 24 THERE ARE 24 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 36 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2004:695455 CAPLUS

DOCUMENT NUMBER: 141:207074

TITLE: Preparation of spirobi[(R)- or (S)-binaphthyl]dimethylammonium derivatives and their use as phase-transfer catalysts for preparation of optically active  $\alpha$ -amino acids

INVENTOR(S): Maruoka, Keiji

PATENT ASSIGNEE(S): Tosoh Corp., Japan

SOURCE: Jpn. Kokai Tokkyo Koho, 49 pp.

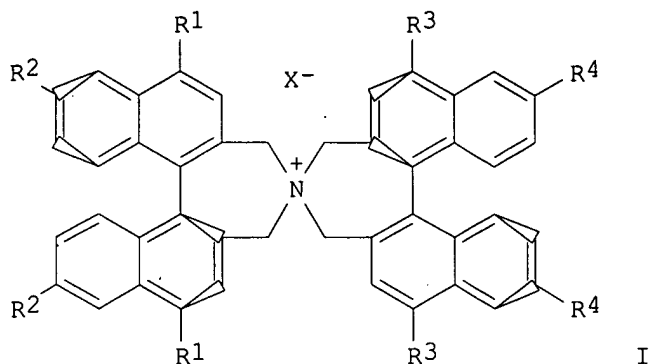
CODEN: JKXXAF

DOCUMENT TYPE: Patent

LANGUAGE: Japanese

FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 2004238362	A	20040826	JP 2003-31361	20030207
PRIORITY APPLN. INFO.:			JP 2003-31361	20030207
OTHER SOURCE(S):	MARPAT 141:207074			
GI				

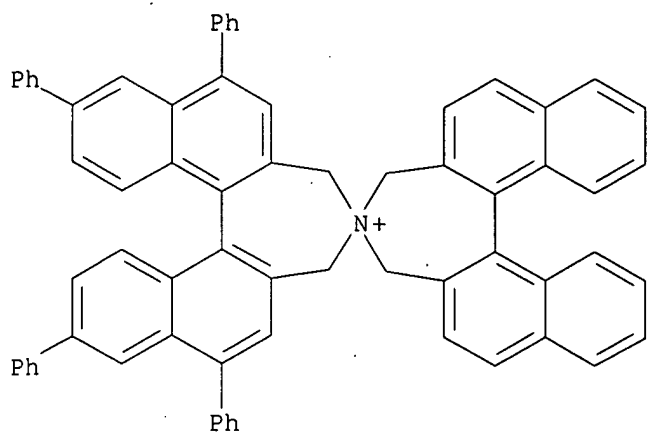


AB Title compds. I [R1-R4 = H, Me, Et, vinyl, ethynyl, C3-10 linear, branched, cyclic alkyl, C5-20 (halo)aryl, etc.; R1-R4 ≠ H; X = halo, thiocyanide, HSO<sub>4</sub>, ClO<sub>4</sub>, PF<sub>6</sub>] are prepared Their intermediates are also claimed. Thus, quaternization of (S)-1,1'-bi-2-bromomethyl-4-phenylnaphthyl with ammonia in a sealed tube gave 42% (S,S)-I (R1 = R3 = Ph, R2 = R4 = H, X = Br). Ph<sub>2</sub>C:NCH<sub>2</sub>CO<sub>2</sub>CMe<sub>3</sub> was alkylated with PhCH<sub>2</sub>Br in PhMe in the presence of the ammonium salt and aqueous KOH at 0° for 6 h to give 86% (R)-Ph<sub>2</sub>C:NCH(CH<sub>2</sub>Ph)CO<sub>2</sub>CMe<sub>3</sub> with 96% ee.

IT 583050-09-3P 583050-11-7P 596107-91-4P  
 596107-92-5P 596107-93-6P 596107-94-7P  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
 USES (Uses)  
 (preparation of optically active spirobi[binaphthyl]dimethylammonium] derivs.  
 as phase-transfer catalysts for preparation of optically active amino acids)

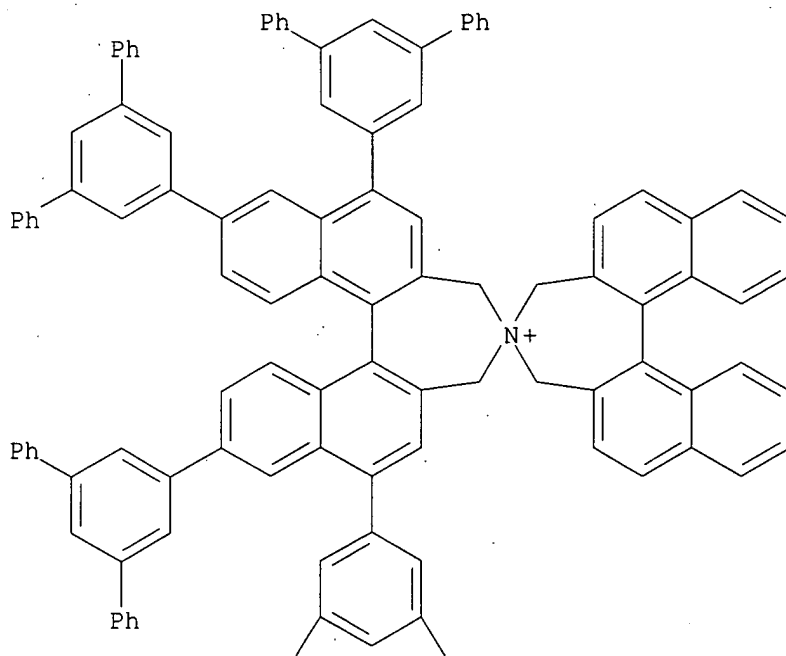
RN 583050-09-3 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
 1,7,9,14-tetraphenyl-, bromide, (11bS,11'bS)- (9CI) (CA INDEX NAME)



RN 583050-11-7 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-1,7,9,14-tetrakis([1,1':3',1''-terphenyl]-5'-yl)-, bromide, (11bS,11'bS)-(9CI) (CA INDEX NAME)

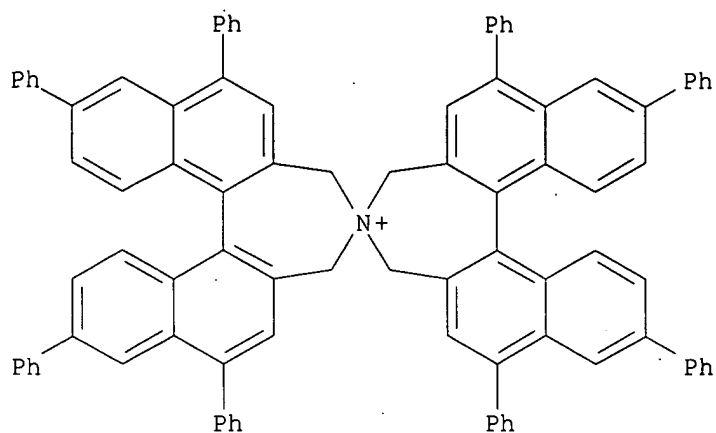
PAGE 1-A



PAGE 2-A

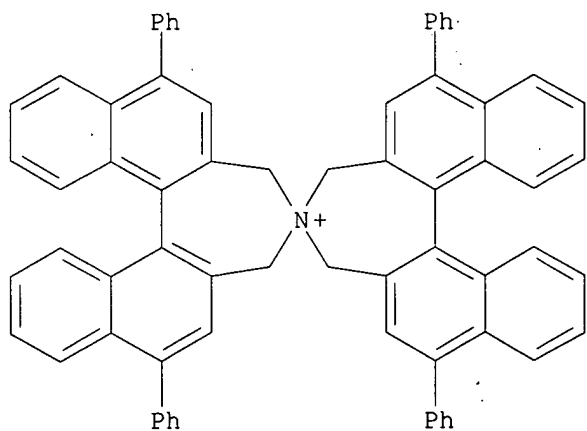


RN 596107-91-4 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-1,1',7,7',9,9',14,14'-octaphenyl-, bromide, (11bS,11'bs)- (9CI) (CA INDEX NAME)



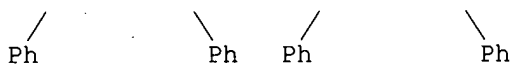
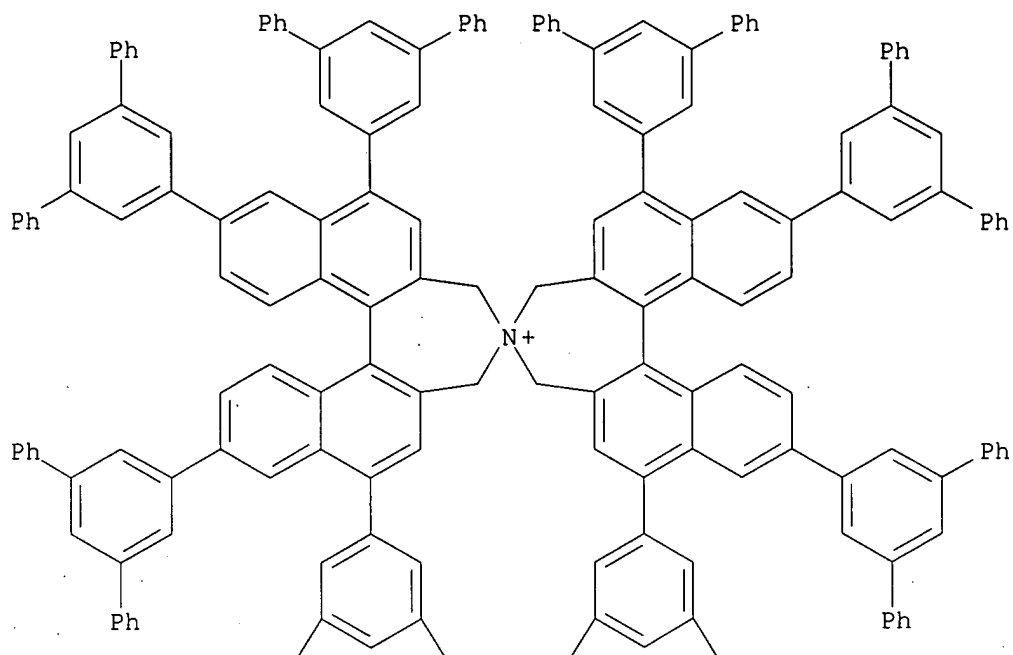
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RN 596107-92-5 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-1,1',7,7'-tetraphenyl-, bromide, (11bS,11'bs)- (9CI) (CA INDEX NAME)



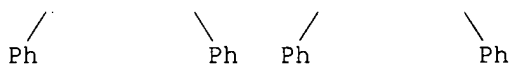
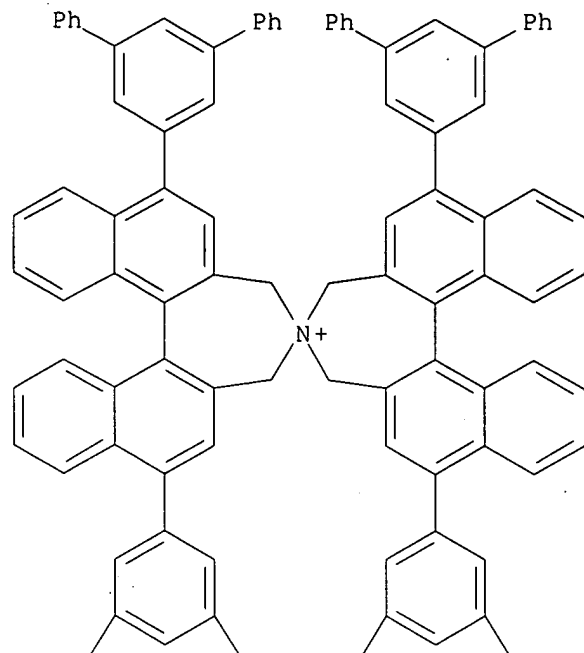
● Br<sup>-</sup>

RN 596107-93-6 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-1,1',7,7',9,9',14,14'-octakis([1,1':3',1''-terphenyl]-5'-yl)-, bromide, (11bS,11'bs)- (9CI) (CA INDEX NAME)



RN 596107-94-7 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
 1,1',7,7'-tetrakis([1,1':3',1''-terphenyl]-5'-yl)-, bromide, (11bS,11'bS)-  
 (9CI) (CA INDEX NAME)





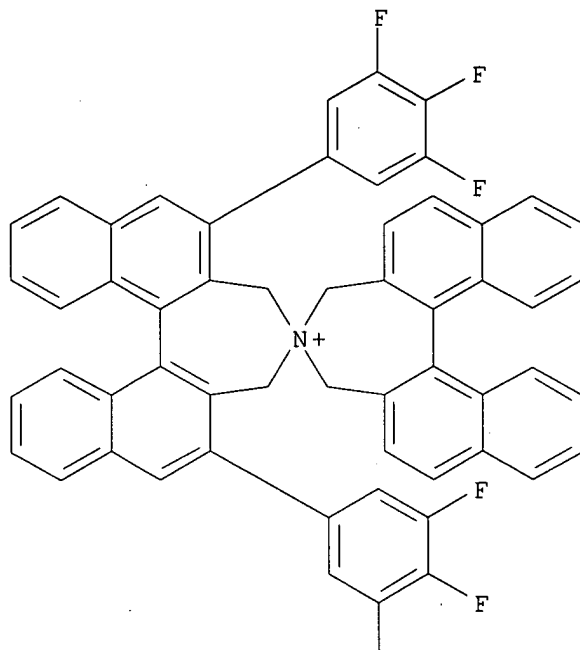
L3 ANSWER 37 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2004:689330 CAPLUS  
 DOCUMENT NUMBER: 141:366435  
 TITLE: Asymmetric alkylation of glycine imine esters using solid supports preloaded with base  
 AUTHOR(S): Yu, Haitao; Takigawa, Setsuko; Koshima, Hideko  
 CORPORATE SOURCE: Department of Applied Chemistry, Faculty of Engineering, Ehime University, Matsuyama, 790-8577, Japan  
 SOURCE: Tetrahedron (2004), 60(38), 8405-8410  
 CODEN: TETRAB; ISSN: 0040-4020  
 PUBLISHER: Elsevier B.V.  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 OTHER SOURCE(S): CASREACT 141:366435  
 AB Investigations into the use of solid supports preloaded with base for the asym. alkylation of a benzophenone-derived glycine-imine under phase-transfer conditions was described. Residual traces of water on the support dramatically accelerated the reactions to complete within a few minutes. The conditions employed in the present synthesis are mild, efficient and general.  
 IT 287384-12-7  
 RL: CAT (Catalyst use); USES (Uses)  
 (synthesis of amino acid Schiff bases by phase-transfer asym.

alkylation of glycine imine ester with alkyl halides catalyzed by  
chiral quaternary ammonium salts on kaolin support preloaded with base)

RN 287384-12-7 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bS)- (CA INDEX  
NAME)

PAGE 1-A



PAGE 2-A

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F

● Br<sup>-</sup>

REFERENCE COUNT: 22 THERE ARE 22 CITED REFERENCES AVAILABLE FOR THIS  
RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 38 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2004:617617 CAPLUS

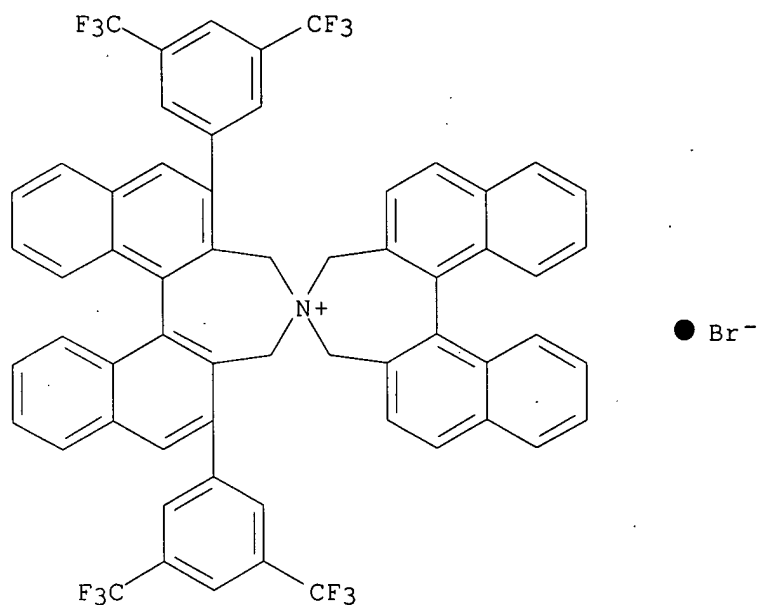
DOCUMENT NUMBER: 141:123455

TITLE: Highly enantioselective construction of quaternary  
stereocenters on  $\beta$ -keto esters by phase-transfer  
catalytic asymmetric alkylation and Michael reaction.  
[Erratum to document cited in CA139:350529]

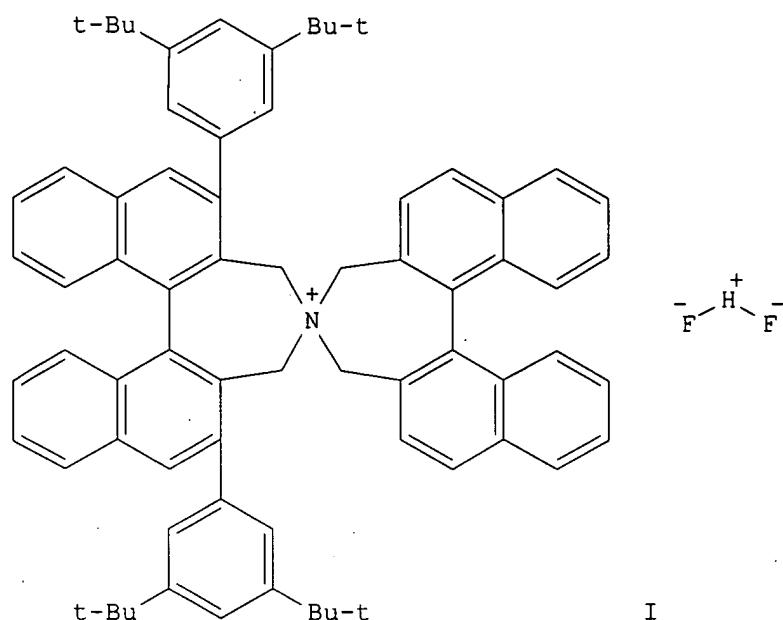
AUTHOR(S): Ooi, Takashi; Miki, Takashi; Taniguchi, Mika;  
Shiraishi, Misato; Takeuchi, Mifune; Maruoka, Keiji  
CORPORATE SOURCE: Department of Chemistry, Kyoto University, Sakyo,  
Kyoto, 606-8502, Japan

SOURCE: Angewandte Chemie, International Edition (2003),  
42(34), 3981  
CODEN: ACIEF5; ISSN: 1433-7851

PUBLISHER: Wiley-VCH Verlag GmbH & Co. KGaA  
DOCUMENT TYPE: Journal  
LANGUAGE: English  
AB In Table 1, for values 80 and 92, entry 7 should be one column to the right, i.e., Yield 80%, Selectivity 92% ee.  
IT 438002-03-0  
RL: CAT (Catalyst use); USES (Uses)  
(stereoselective preparation of  $\alpha$ -alkyl  $\beta$ -keto esters via phase-transfer-catalyzed asym. alkylation of  $\beta$ -keto esters with di-Me sulfate or alkyl bromides (Erratum))  
RN 438002-03-0 CAPLUS  
CN 8,8'-Spirobi[8H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



L3 ANSWER 39 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
ACCESSION NUMBER: 2004:586239 CAPLUS  
DOCUMENT NUMBER: 141:260338  
TITLE: Evaluation of the relationship between the catalyst structure and regio- as well as stereoselectivity in the chiral ammonium bifluoride-catalyzed asymmetric addition of silyl nitronates to  $\alpha,\beta$ -unsaturated aldehydes  
AUTHOR(S): Ooi, Takashi; Morimoto, Kumiko; Doda, Kanae; Maruoka, Keiji  
CORPORATE SOURCE: Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto, 606-8502, Japan  
SOURCE: Chemistry Letters (2004), 33(7), 824-825  
CODEN: CMLTAG; ISSN: 0366-7022  
PUBLISHER: Chemical Society of Japan  
DOCUMENT TYPE: Journal  
LANGUAGE: English  
OTHER SOURCE(S): CASREACT 141:260338  
GI



AB Unique relationship between the catalyst structure and regio- and stereoselectivity in the chiral quaternary ammonium bifluoride-catalyzed asym. addition of silyl nitronates to  $\alpha,\beta$ -unsatd. aldehydes has been reported. E.g., chiral catalyst (R,R)-I catalyzed the addition of TMSO(O):CH<sub>2</sub>Et and (E)-PhCH:CHCHO to give 99% (19:1) O<sub>2</sub>NCH<sub>2</sub>EtCHPhCH<sub>2</sub>CHO (II) and (E)-PhCH:CHCH(OH)CH<sub>2</sub>EtNO<sub>2</sub> (76:24 syn/anti for II and 94% ee for (3S,4R)-syn-II).

IT 586344-89-0 586344-91-4 756511-42-9  
 756511-45-2 756511-48-5 756511-52-1  
 756511-55-4 756511-58-7 756511-61-2  
 756512-74-0

RL: CAT (Catalyst use); USES (Uses)

(regio- and enantioselective Michael addition of silyl nitronates to  $\alpha,\beta$ -unsatd. aldehydes catalyzed by chiral quaternary ammonium bifluorides)

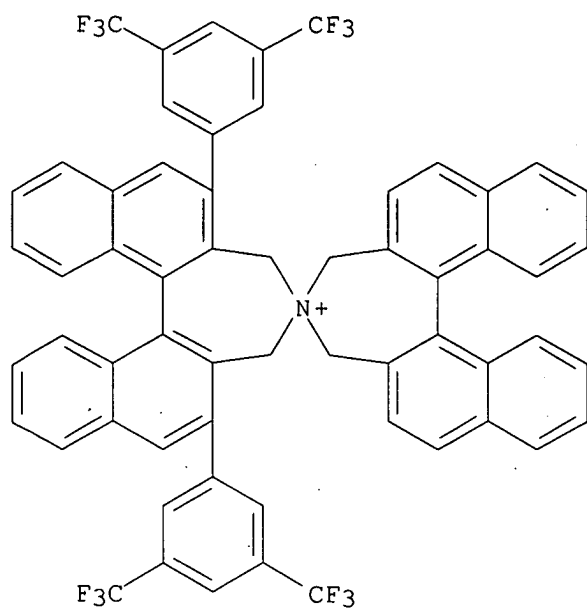
RN 586344-89-0 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, (11bR,11'bR)-, (hydrogen difluoride) (1:1) (CA INDEX NAME)

CM 1

CRN 586344-88-9

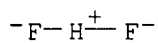
CMF C60 H36 F12 N



CM 2

CRN 18130-74-0

CMF F2 H



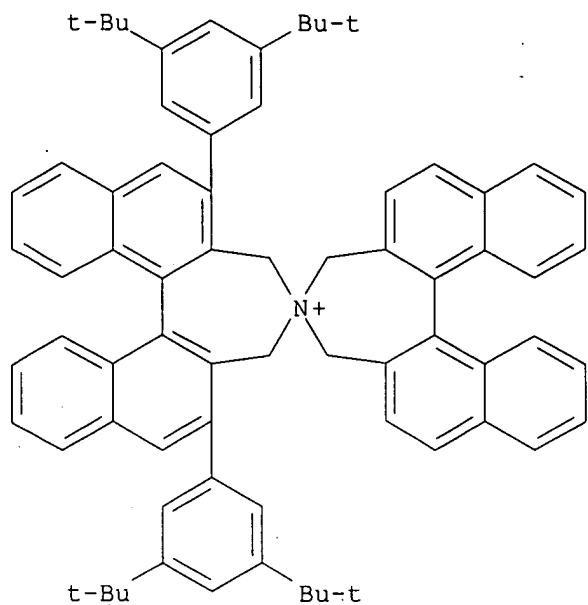
RN 586344-91-4 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(1,1-dimethylethyl)phenyl]-3,3',5,5'-tetrahydro-, (11bR,11'bR)-, (hydrogen difluoride) (1:1) (CA INDEX NAME)

CM 1

CRN 586344-90-3

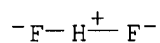
CMF C72 H72 N



CM 2

CRN 18130-74-0

CMF F2 H



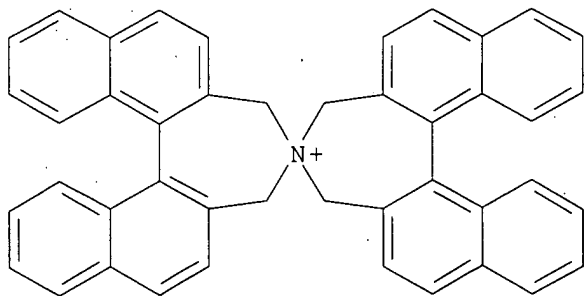
RN 756511-42-9 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-, (11bR,11'bR)-, (hydrogen difluoride) (9CI) (CA INDEX NAME)

CM 1

CRN 756511-41-8

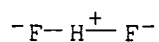
CMF C44 H32 N



CM 2

CRN 18130-74-0

CMF F2 H



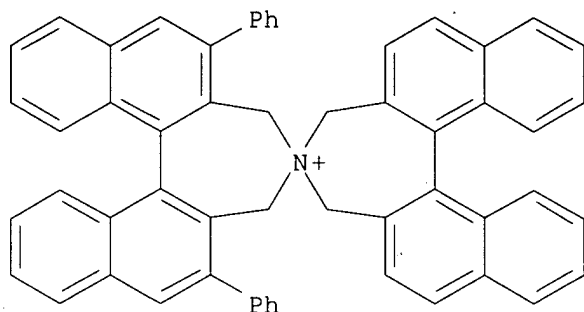
RN 756511-45-2 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-diphenyl-, (11bR,11'bR)-, (hydrogen difluoride) (9CI) (CA INDEX NAME)

CM 1

CRN 756511-44-1

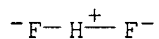
CMF C56 H40 N



CM 2

CRN 18130-74-0

CMF F2 H



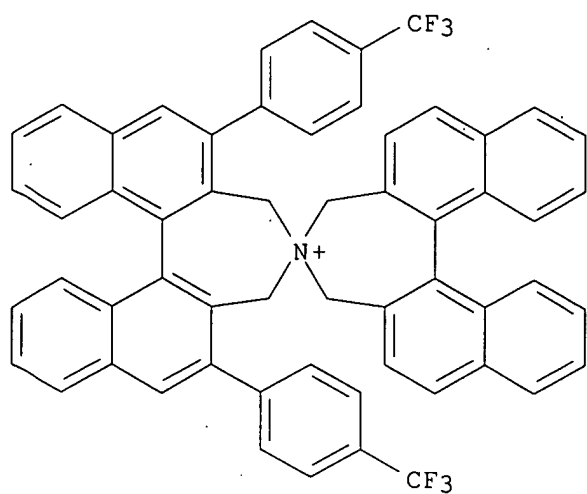
RN 756511-48-5 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[4-(trifluoromethyl)phenyl]-, (11bR,11'bR)-, (hydrogen difluoride) (9CI) (CA INDEX NAME)

CM 1

CRN 756511-47-4

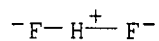
CMF C58 H38 F6 N



CM 2

CRN 18130-74-0

CMF F2 H



RN 756511-52-1 .CAPLUS

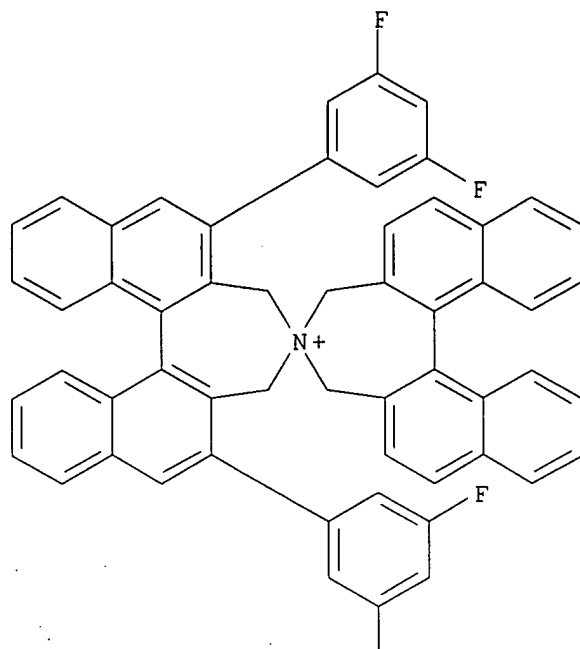
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis(3,5-difluorophenyl)-3,3',5,5'-tetrahydro-, (11bR,11'bR)-, (hydrogen difluoride) (9CI) (CA INDEX NAME)

CM 1

CRN 756511-51-0

CMF C56 H36 F4 N

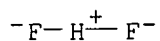




CM 2

CRN 18130-74-0

CMF F2 H



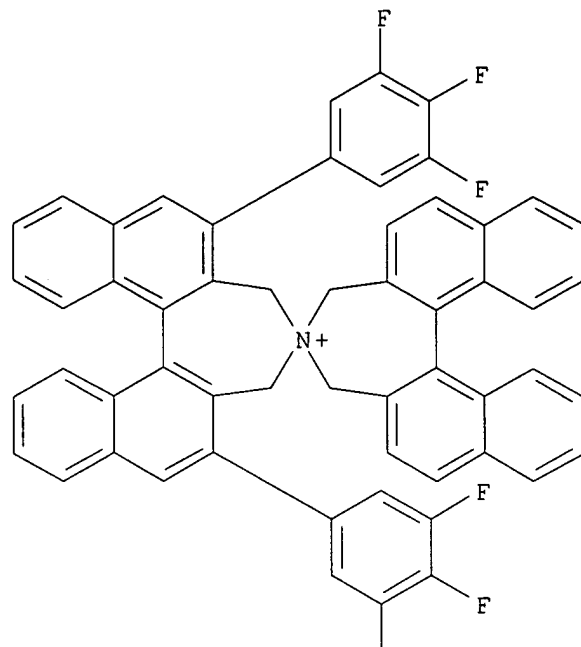
RN 756511-55-4 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, (11bR,11'bR)-, (hydrogen difluoride) (9CI) (CA INDEX NAME)

CM 1

CRN 756511-54-3

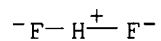
CMF C56 H34 F6 N



CM 2

CRN 18130-74-0

CMF F2 H



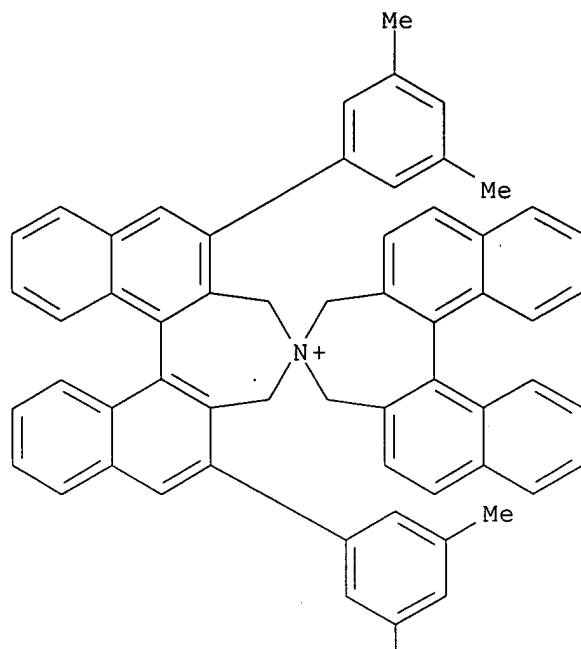
RN 756511-58-7 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis(3,5-dimethylphenyl)-3,3',5,5'-tetrahydro-, (11bR,11'bR)-, (hydrogen difluoride) (9CI) (CA INDEX NAME)

CM 1

CRN 756511-57-6

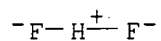
CMF C60 H48 N



CM 2

CRN 18130-74-0

CMF F2 H



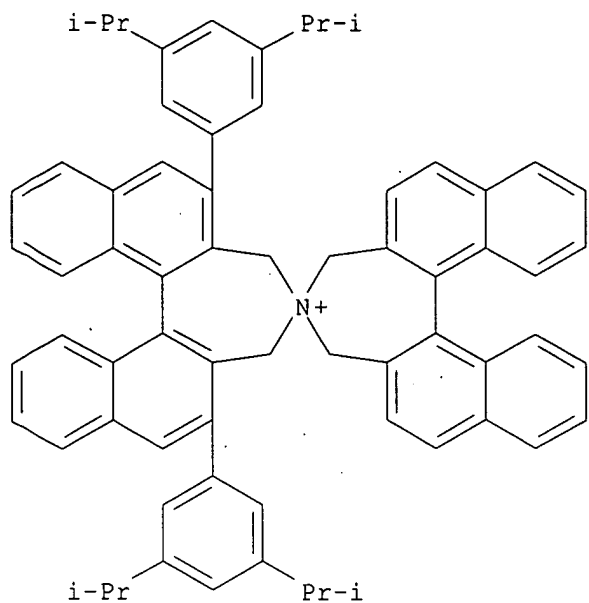
RN 756511-61-2 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(1-methylethyl)phenyl]-3,3',5,5'-tetrahydro-, (11bR,11'bR)-, (hydrogen difluoride) (9CI) (CA INDEX NAME)

CM 1

CRN 756511-60-1

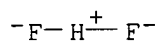
CMF C68 H64 N



CM 2

CRN 18130-74-0

CMF F2 H



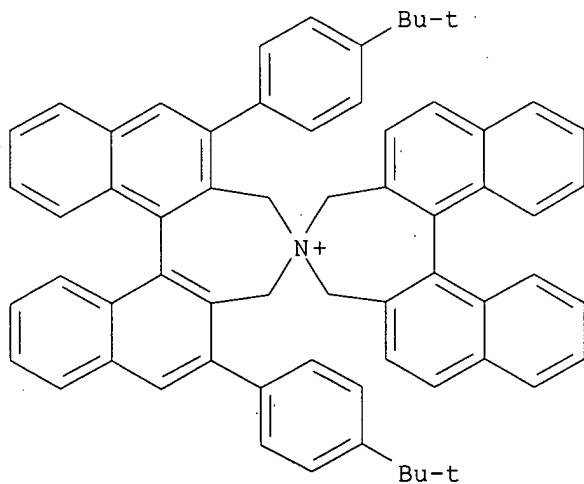
RN 756512-74-0 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[4-(1,1-dimethylethyl)phenyl]-3,3',5,5'-tetrahydro-, (11bR,11'bR)-, (hydrogen difluoride) (9CI) (CA INDEX NAME)

CM 1

CRN 756512-73-9

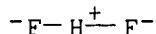
CMF C64 H56 N



CM 2

CRN 18130-74-0

CMF F2 H



REFERENCE COUNT: 20 THERE ARE 20 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 40 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2004:566817 CAPLUS

DOCUMENT NUMBER: 141:277027

TITLE: Development of Highly Diastereo- and Enantioselective Direct Asymmetric Aldol Reaction of a Glycinate Schiff Base with Aldehydes Catalyzed by Chiral Quaternary Ammonium Salts

AUTHOR(S): Ooi, Takashi; Kameda, Minoru; Taniguchi, Mika; Maruoka, Keiji

CORPORATE SOURCE: Department of Chemistry Graduate School of Science, Kyoto University, Kyoto, 606-8502, Japan

SOURCE: Journal of the American Chemical Society (2004), 126(31), 9685-9694

CODEN: JACSAT; ISSN: 0002-7863

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 141:277027

AB A highly efficient direct asym. aldol reaction of a glycinate Schiff base with aldehydes has been achieved under mild organic/aqueous biphasic conditions with excellent stereochem. control, using a chiral quaternary ammonium salt as a phase-transfer catalyst. The initially developed reaction conditions, using 2 equiv of aqueous base (1% NaOH), exhibited inexplicably limited general applicability in terms of aldehyde acceptors. The mechanistic investigation revealed the intervention of an unfavorable yet inevitable retro aldol process involving the chiral catalyst. On the basis of this information, a reliable procedure has been established by use of a catalytic amount of 1% aq NaOH and ammonium chloride, which tolerates a wide range of aldehydes to afford anti- $\beta$ -hydroxy- $\alpha$ -amino esters almost exclusively in an essentially optically pure form.

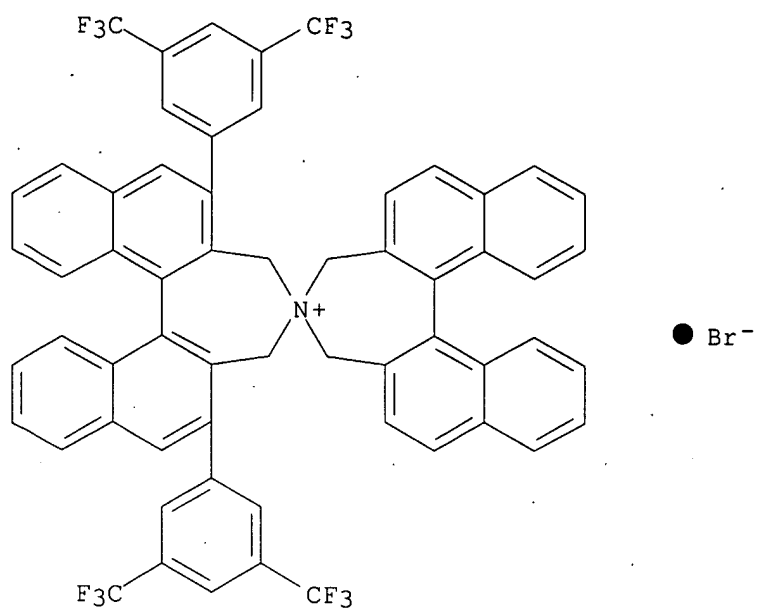
IT 515137-97-0 515137-98-1 757246-08-5  
757246-09-6

RL: CAT (Catalyst use); USES (Uses)

(stereoselective direct asym. aldol reaction of a glycinate Schiff base with aldehydes catalyzed by chiral quaternary ammonium salts)

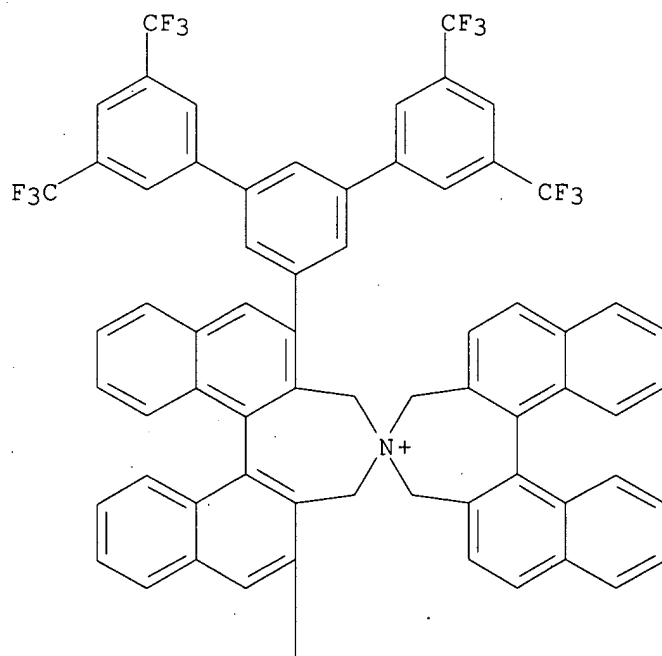
RN 515137-97-0 CAPLUS

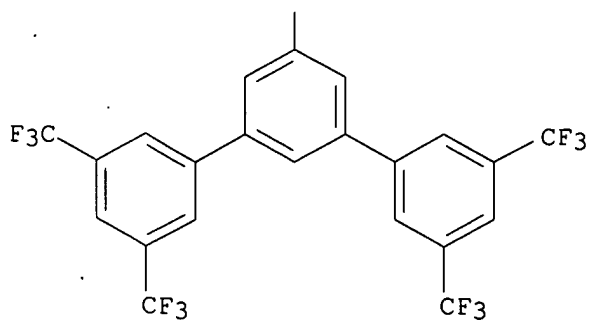
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide (1:1), (11bR,11'bR)- (CA INDEX NAME)



RN 515137-98-1 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
 2,6-bis[3,3'',5,5''-tetrakis(trifluoromethyl)[1,1':3',1''-terphenyl]-5'-  
 yl]-, bromide, (11bR,11'bR)- (9CI) (CA INDEX NAME)

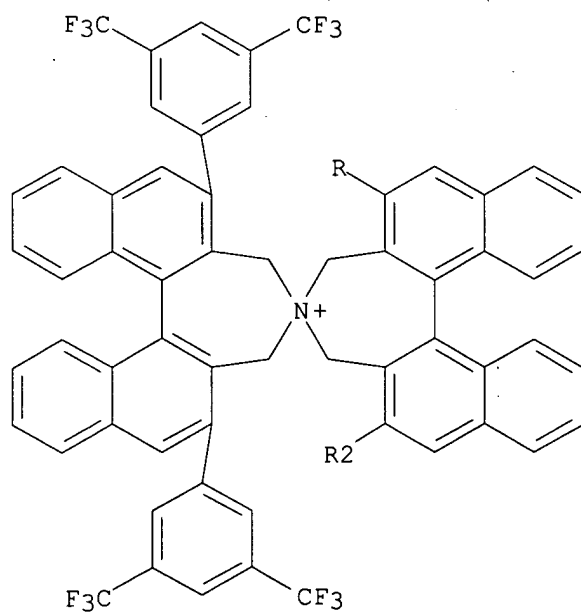
PAGE 1-A

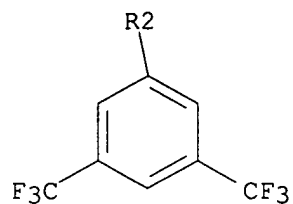
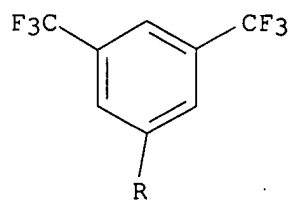




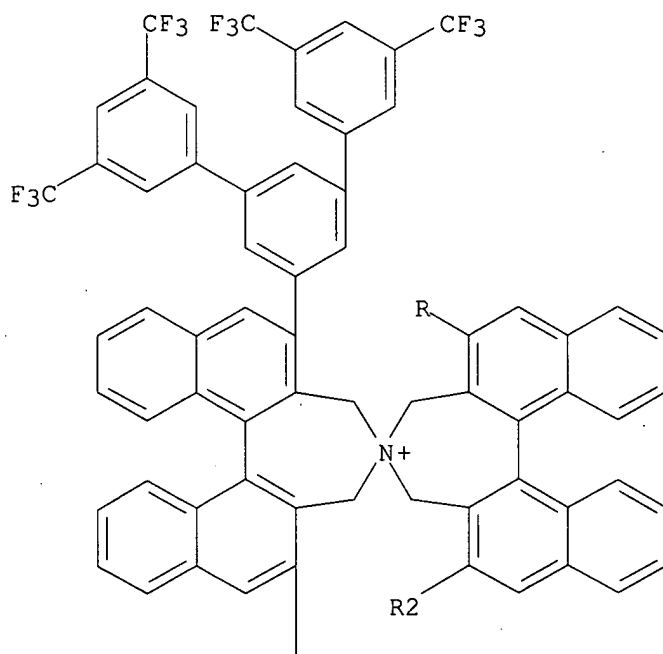
RN 757246-08-5 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,2',6,6'-tetrakis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide, (11bR,11'bR)-(9CI) (CA INDEX NAME)



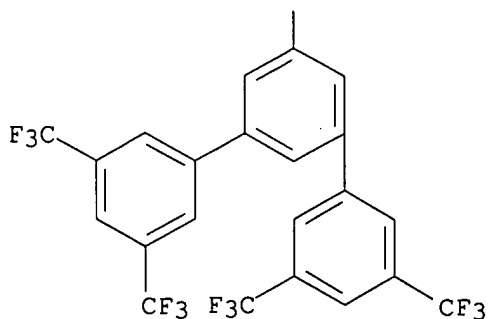


RN 757246-09-6 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
 2,2',6,6'-tetrakis[3,3'',5,5''-tetrakis(trifluoromethyl)[1,1':3,1''-  
 terphenyl]-5'-yl]-, bromide, (11bR,11'bR)- (9CI) (CA INDEX NAME)

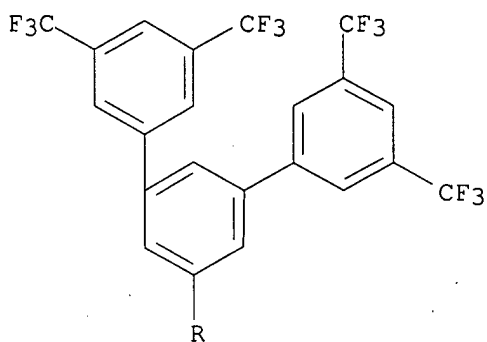




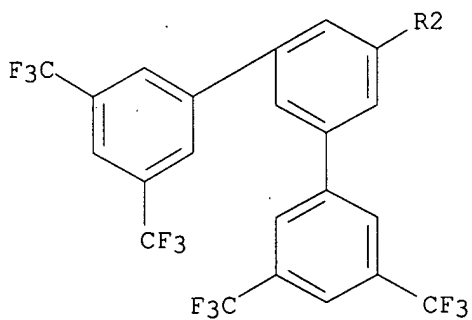
PAGE 2-A



PAGE 3-A



PAGE 4-A



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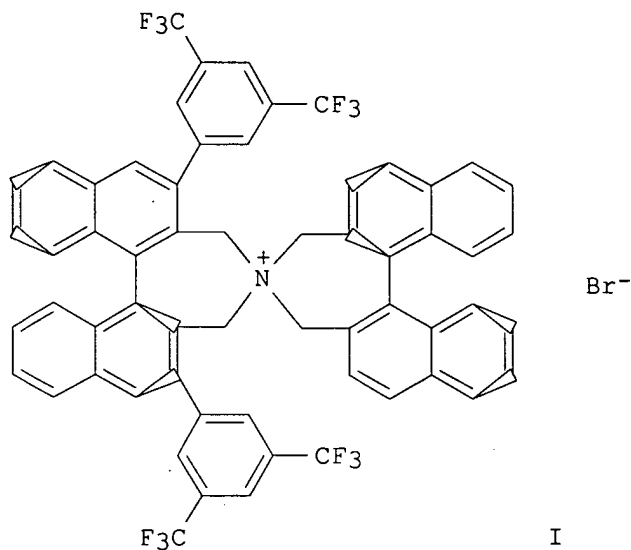
REFERENCE COUNT: 83 THERE ARE 83 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 41 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
ACCESSION NUMBER: 2004:507804 CAPLUS  
DOCUMENT NUMBER: 141:54074  
TITLE: Stereoselective alkylation of  $\beta$ -keto esters using asymmetric quaternary ammonium catalysts  
INVENTOR(S): Maruoka, Keiji  
PATENT ASSIGNEE(S): Nagae & Co., Ltd., Japan  
SOURCE: Jpn. Kokai Tokkyo Koho, 18 pp.  
CODEN: JKXXAF

DOCUMENT TYPE: Patent  
 LANGUAGE: Japanese  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 2004175758	A	20040624	JP 2002-346403	20021128
PRIORITY APPLN. INFO.:			JP 2002-346403	20021128
OTHER SOURCE(S):	MARPAT	141:54074		

GI



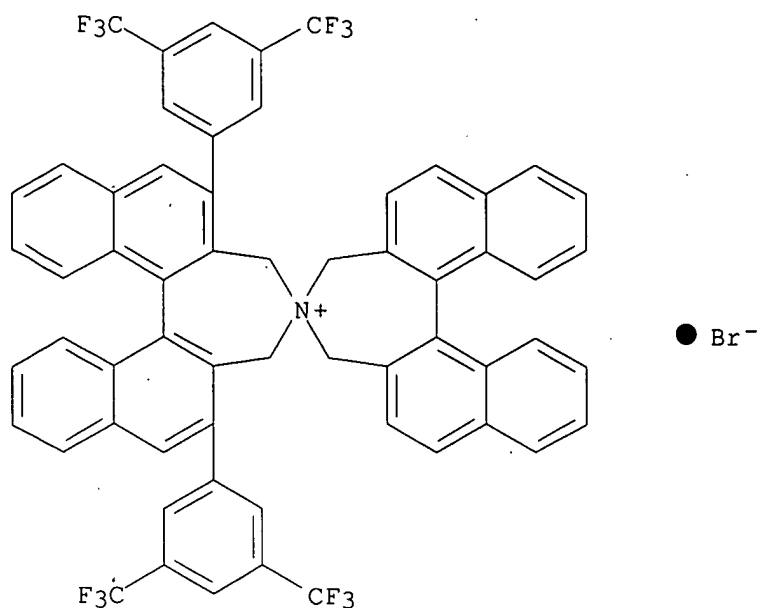
AB Optically active ACOCBR1CO2R [A = (un)substituted aromatic hydrocarbyl, (un)substituted C1-4 alkyl; B, R = C1-4 (halo)alkyl; AB may form ring; R1 = (un)substituted C1-4 alkyl, (un)substituted C2-6 alkenyl] are prepared by alkylation of ACOCHBCO2R (A, B, R = same as above) by alkyl sulfates or R1X1 (R1 = same as above; X1 = leaving group) in the presence of bases and axially asym. quaternary ammonium salts I [Ar1, Ar2 = (un)substituted aryl, (un)substituted heteroaryl]. 2-(Tert-butoxycarbonyl)-1-indanone was alkylated by PhCH2Br in PhMe in the presence of (S,S)-I [Ar1 = Ar2 = 3,5-bis(trifluoromethyl)phenyl, X = Br] and CsOH at -40° for 3 h to give 90% 2-benzyl-2-(tert-butoxycarbonyl)-1-indanone with 95% ee.

IT 438002-03-0

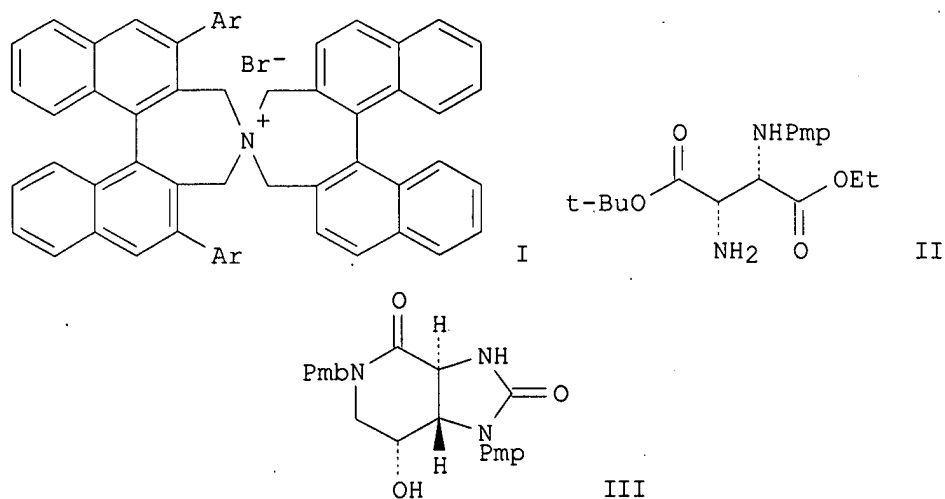
RL: CAT (Catalyst use); USES (Uses)  
 (stereoselective alkylation of  $\beta$ -keto esters using asym.  
 quaternary ammonium catalysts and bases)

RN 438002-03-0 CAPLUS

CN 8,8'-Spirobi[8H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



L3 ANSWER 42 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2004:482335 CAPLUS  
 DOCUMENT NUMBER: 141:191014  
 TITLE: Catalytic Asymmetric Synthesis of a Nitrogen Analogue  
 of Dialkyl Tartrate by Direct Mannich Reaction under  
 Phase-Transfer Conditions  
 AUTHOR(S): Ooi, Takashi; Kameda, Minoru; Fujii, Junichi; Maruoka,  
 Keiji  
 CORPORATE SOURCE: Department of Chemistry, Graduate School of Science,  
 Kyoto University, Kyoto, 606-8502, Japan  
 SOURCE: Organic Letters (2004), 6(14), 2397-2399  
 CODEN: ORLEF7; ISSN: 1523-7060  
 PUBLISHER: American Chemical Society  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 OTHER SOURCE(S): CASREACT 141:191014  
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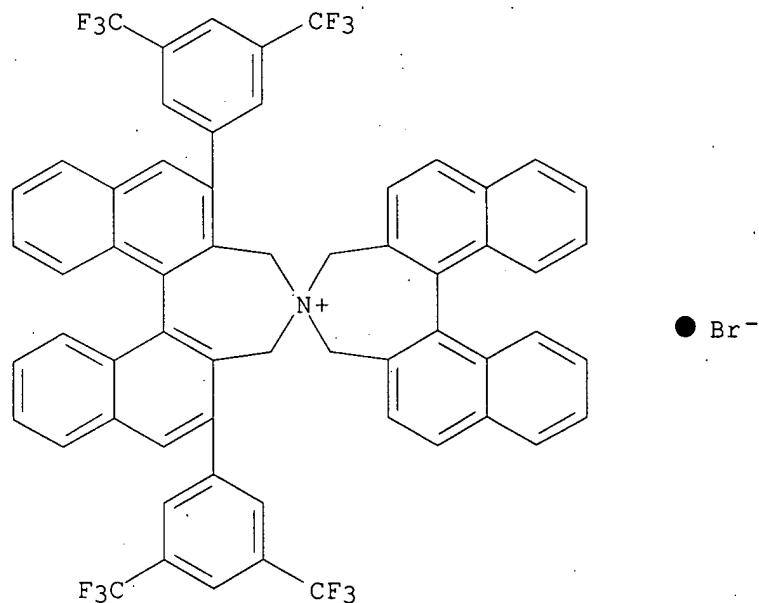


AB Mannich reaction of glycinate Schiff base  $\text{Ph}_2\text{C:NCH}_2\text{CO}_2\text{Bu-t}$  with  $\text{PmpN:CHCO}_2\text{Et}$  (Pmp = p-methoxyphenyl) has been accomplished with high enantioselectivity by the utilization of N-spiro C2-sym. quaternary ammonium bromide (R,R)-I [Ar = 3,5-bis(trifluoromethyl)phenyl, 3,4,5-trifluorophenyl, 3,5-bis(3,4,5-trifluorophenyl)phenyl] as a phase transfer catalyst. The product aminoaspartate II was obtained in 88% yield (82:18 ratio of syn:anti; 91% enantiomeric excess of syn product) with catalyst I (Ar = 3,4,5-trifluorophenyl). This methodol. enables the catalytic asym. synthesis of differentially protected 3-aminoaspartate, a nitrogen analog of dialkyl tartrate. II was converted in five steps into bicyclic hydroxy dione III (Pmb = p-methoxybenzyl), a precursor of streptolidine lactam.

IT 515137-97-0 534570-50-8 736974-91-7  
 RL: CAT (Catalyst use); USES (Uses)  
 (asym. preparation of aminoaspartate by Mannich reaction of glycinate Schiff base with an iminoacetate in presence of chiral ammonium phase transfer catalysts)

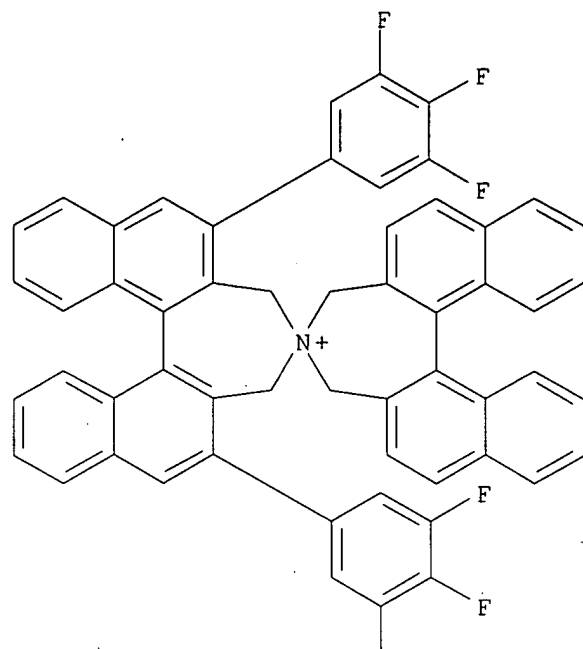
RN 515137-97-0 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide (1:1), (11bR,11'bR)- (CA INDEX NAME)

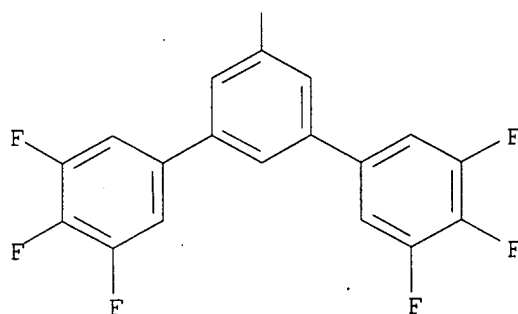
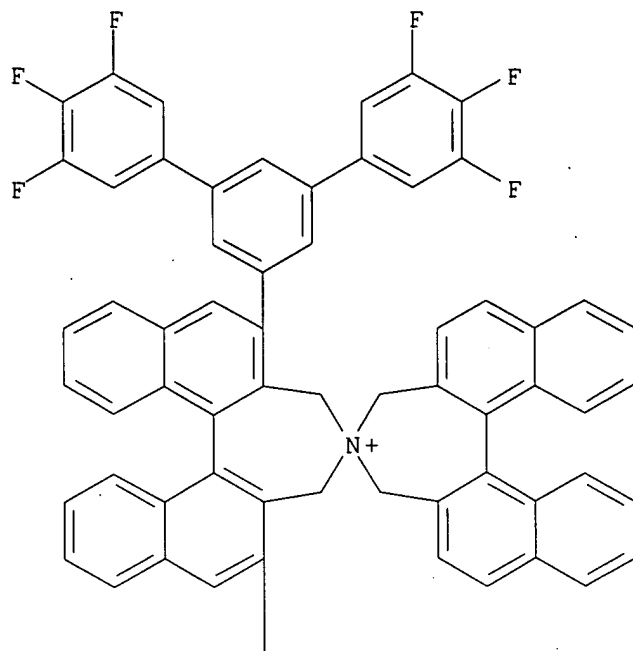


RN 534570-50-8 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bR,11'bR)- (CA INDEX NAME)



RN 736974-91-7 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis(3,3'',4,4'',5,5''-hexafluoro[1,1':3',1''-terphenyl]-5'-yl)-3,3',5,5'-tetrahydro-, bromide, (11bR,11'bR)- (9CI) (CA INDEX NAME)



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REFERENCE COUNT: 28 THERE ARE 28 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 43 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2004:410270 CAPLUS.

DOCUMENT NUMBER: 141:106712

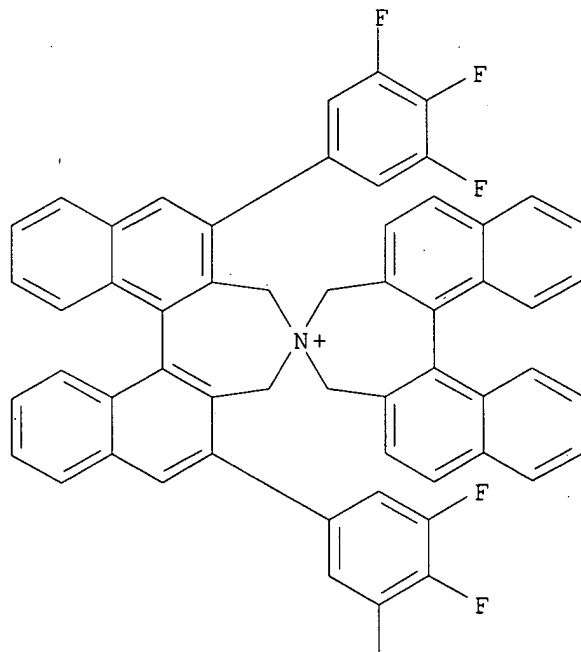
TITLE: Highly enantioselective phase-transfer-catalytic alkylation of 2-phenyl-2-oxazoline-4-carboxylic acid tert-butyl ester for the asymmetric synthesis of  $\alpha$ -alkyl serines

AUTHOR(S): Jew, Sang-sup; Lee, Yeon-Ju; Lee, Jihye; Kang, Myoung Joo; Jeong, Byeong-Seon; Lee, Jeong-Hee; Yoo, Mi-Sook; Kim, Mi-Jeong; Choi, Sea-hoon; Ku, Jin-Mo; Park, Hyeung-geun

CORPORATE SOURCE: Research Institute of Pharmaceutical Sciences and College of Pharmacy, Seoul National University, Seoul,

SOURCE: 151-742, S. Korea  
 Angewandte Chemie, International Edition (2004),  
 43(18), 2382-2385  
 CODEN: ACIEF5; ISSN: 1433-7851  
 PUBLISHER: Wiley-VCH Verlag GmbH & Co. KGaA .  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 OTHER SOURCE(S): CASREACT 141:106712  
 AB A facile synthesis of chiral  $\alpha$ -alkyl serines  $\text{H}_2\text{NCR}(\text{CH}_2\text{OH})\text{CO}_2\text{H}$  [R = Et, allyl; 2-methylallyl, propargyl, (un)substituted benzyl or 2-naphthylmethyl] involves the asym. alkylation of 2-phenyl-2-oxazoline-4-carboxylic acid tert-Bu ester with alkyl halides (RX) under phase-transfer catalysis (PTC), followed by acidic hydrolysis of the alkylation products. The phenyloxazoline moiety enhances the acidity of the  $\alpha$  proton of the ester and is an excellent protecting group for both the amino and hydroxy functions of the serine ester.  
 IT 287384-12-7  
 RL: CAT (Catalyst use); USES (Uses)  
 (enantioselective phase-transfer catalytic alkylation of phenyloxazolinecarboxylate for asym. synthesis of  $\alpha$ -alkyl serines)  
 RN 287384-12-7 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)

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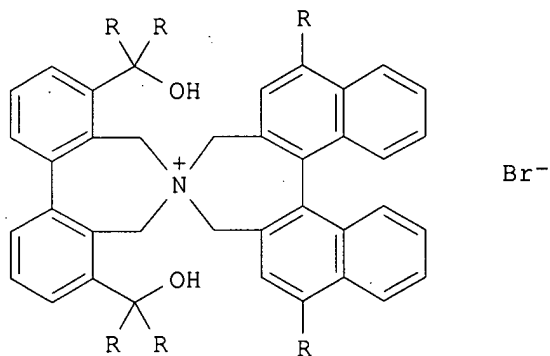
PAGE 2-A

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● Br<sup>-</sup>

REFERENCE COUNT: 61 THERE ARE 61 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 44 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
ACCESSION NUMBER: 2004:400619 CAPLUS  
DOCUMENT NUMBER: 141:140245  
TITLE: Design of New Chiral Phase-Transfer Catalysts with Dual Functions for Highly Enantioselective Epoxidation of  $\alpha,\beta$ -Unsaturated Ketones  
AUTHOR(S): Ooi, Takashi; Ohara, Daisuke; Tamura, Masazumi; Maruoka, Keiji  
CORPORATE SOURCE: Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto, 606-8502, Japan  
SOURCE: Journal of the American Chemical Society (2004), 126(22), 6844-6845  
CODEN: JACSAT; ISSN: 0002-7863  
PUBLISHER: American Chemical Society  
DOCUMENT TYPE: Journal  
LANGUAGE: English  
OTHER SOURCE(S): CASREACT 141:140245  
GI

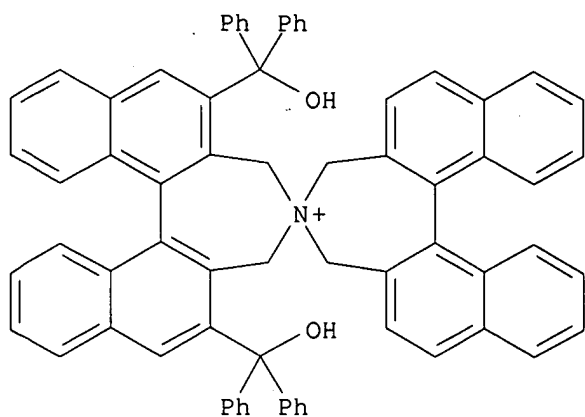


AB A new chiral ammonium bromide I ( $R = 3,5\text{-Ph}_2\text{C}_6\text{H}_3$ ), possessing diarylmethanol functionality as a substrate recognition site, has been designed as a promising, dual-functioning catalyst for the highly enantioselective epoxidn. of  $\alpha,\beta$ -unsatd. ketones under mild phase-transfer conditions. For instance, vigorous stirring of a mixture of chalcone, I (3 mol %), and 13% NaOCl in toluene at  $0^\circ$  for 24 h gave epoxy chalcone quant. with 96% ee. A variety of  $\alpha,\beta$ -unsatd. ketones can also be epoxidized with rigorous stereochem. control, clearly demonstrating the effectiveness and utility of the present system. Further, a successful single-crystal X-ray diffraction anal. of hexafluorophosphate analog of I uncovered its distinctive three-dimensional mol. architecture and provided useful information for postulating the transition state.

IT 727713-02-2P 727713-03-3P 727713-04-4P  
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
USES (Uses)  
(asym. epoxidn. of  $\alpha,\beta$ -unsatd. ketones using chiral quaternary ammonium bromides as phase-transfer catalysts with dual functions)

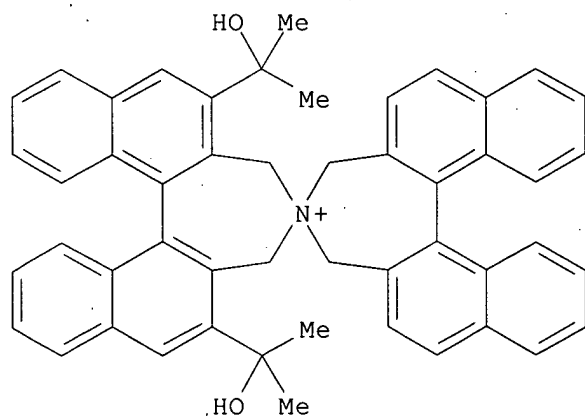
RN 727713-02-2 CAPLUS  
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(hydroxydiphenylmethyl)-, bromide, (11bR,11'BS)- (9CI) (CA INDEX NAME)





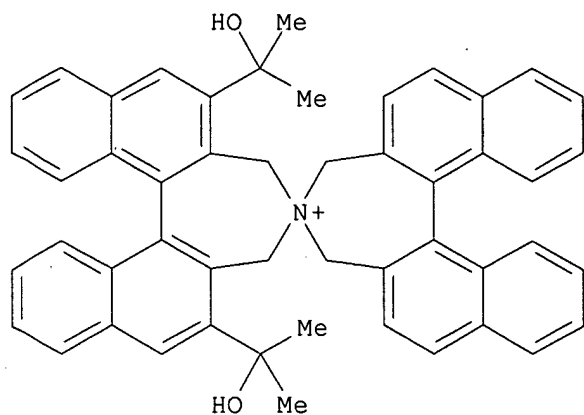
● Br<sup>-</sup>

RN 727713-03-3 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(1-hydroxy-1-methylethyl)-, bromide, (11bR,11'BS)- (9CI) (CA INDEX NAME)



● Br<sup>-</sup>

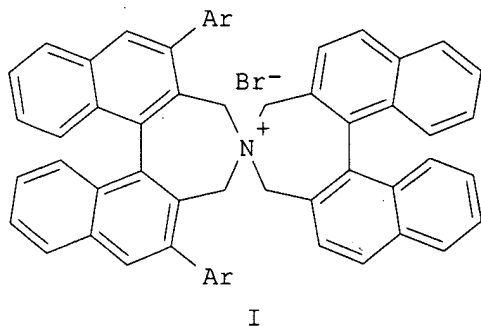
RN 727713-04-4 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(1-hydroxy-1-methylethyl)-, bromide, (11bS,11'BS)- (9CI) (CA INDEX NAME)



● Br<sup>-</sup>

REFERENCE COUNT: 21 THERE ARE 21 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 45 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2004:356397 CAPLUS  
 DOCUMENT NUMBER: 141:123890  
 TITLE: Stereoselective terminal functionalization of small peptides for catalytic asymmetric synthesis of unnatural peptides  
 AUTHOR(S): Maruoka, Keiji; Tayama, Eiji; Ooi, Takashi  
 CORPORATE SOURCE: Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto, 606-8502, Japan  
 SOURCE: Proceedings of the National Academy of Sciences of the United States of America (2004), 101(16), 5824-5829  
 CODEN: PNASA6; ISSN: 0027-8424  
 PUBLISHER: National Academy of Sciences  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 OTHER SOURCE(S): CASREACT 141:123890  
 GI



AB The asym. phase-transfer catalytic alkylation of peptides has been achieved by the use of designed C2-sym. chiral quaternary ammonium bromides (S,S)- and (R,R)-I [Ar = 2-naphthyl, 3,4,5-trifluorophenyl, 3,5-di-tert-butylphenyl, 3,5-bis(3,5-di-tert-butylphenyl)phenyl] as

catalysts. Excellent stereoselectivities were uniformly observed in the alkylation with a variety of alkyl halides and the efficiency of the transmission of stereochem. information was not affected by the side-chain structure of the preexisting amino acid residues. This method also enables an asym. construction of noncoded  $\alpha,\alpha$ -dialkyl- $\alpha$ -amino acid residues at the peptide terminal. Since this chirality can be efficiently transferred to the adjacent amino acid moiety, our approach provides a general procedure not only for the highly stereoselective terminal functionalization of peptides but also for the sequential asym. construction of unnatural oligopeptides, which should play a vital role in the peptide-based drug discovery process.

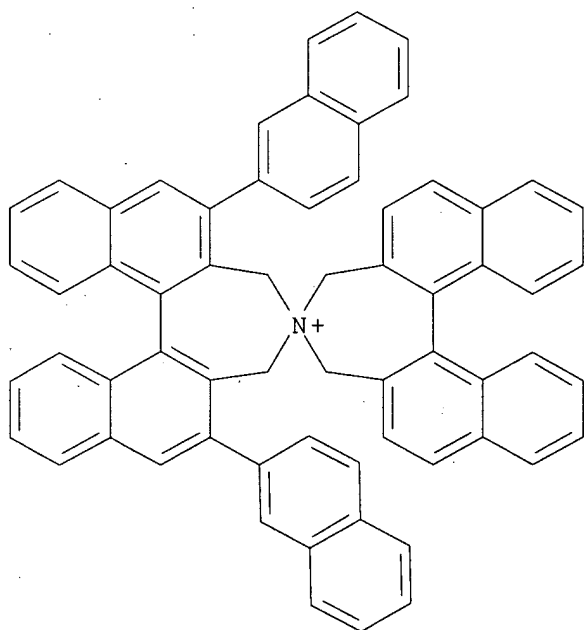
IT 237762-42-4 287384-12-7 466679-91-4  
501934-20-9 501934-21-0 534576-68-6  
724425-22-3

RL: CAT (Catalyst use); USES (Uses)

(asym. phase-transfer catalytic alkylation of peptides using designed C2-sym. chiral quaternary ammonium bromides)

RN 237762-42-4 CAPLUS

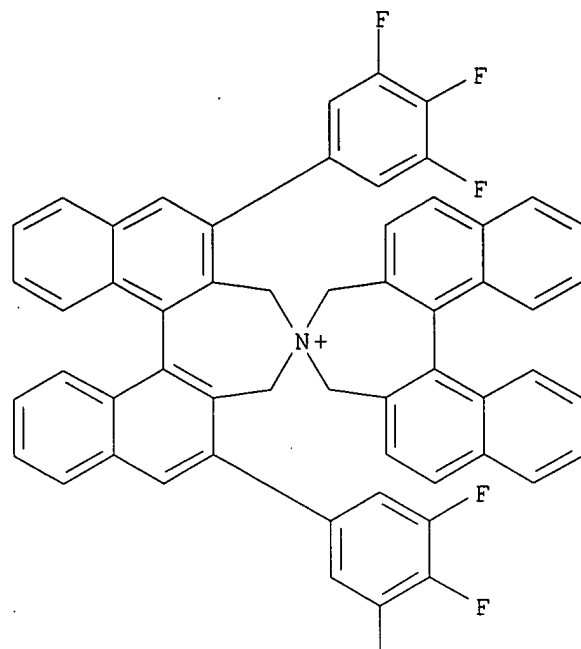
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-di-2-naphthalenyl-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



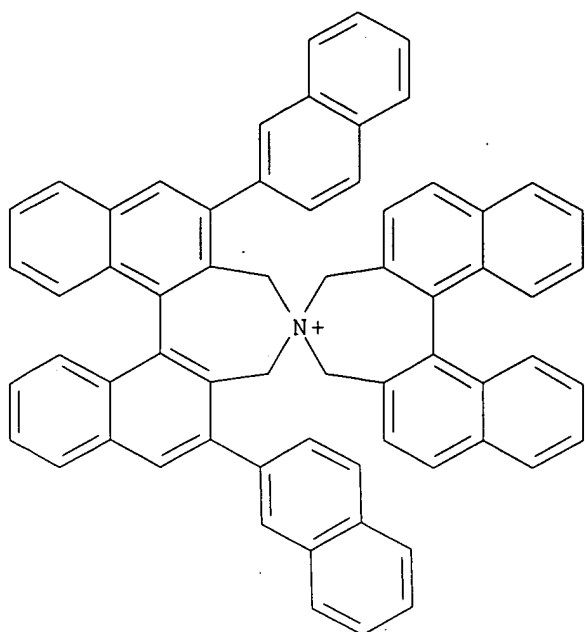
● Br<sup>-</sup>

RN 287384-12-7 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



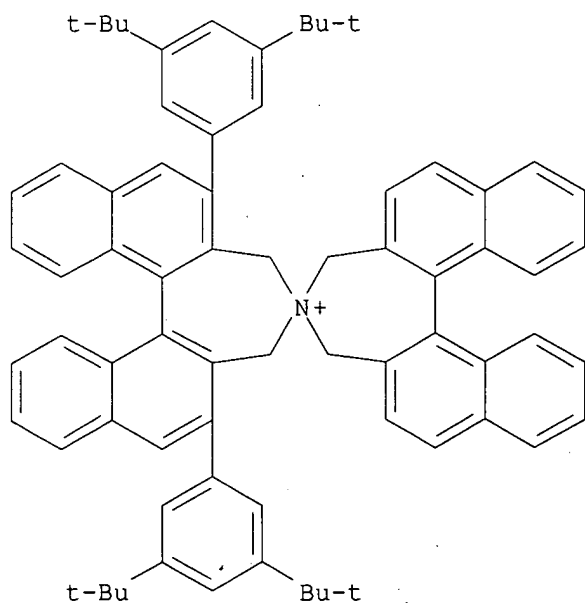
RN 466679-91-4 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
 2,6-di-2-naphthalenyl-, bromide, (11bR,11'bR)- (9CI) (CA INDEX NAME)



● Br<sup>-</sup>

RN 501934-20-9 CAPLUS

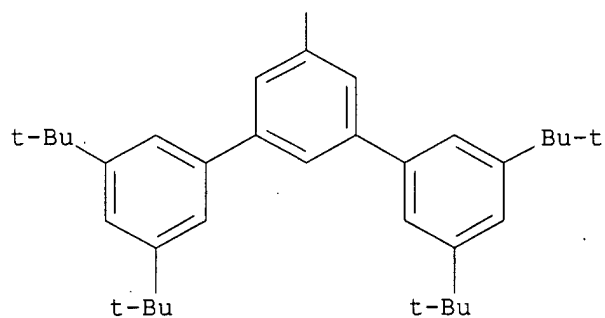
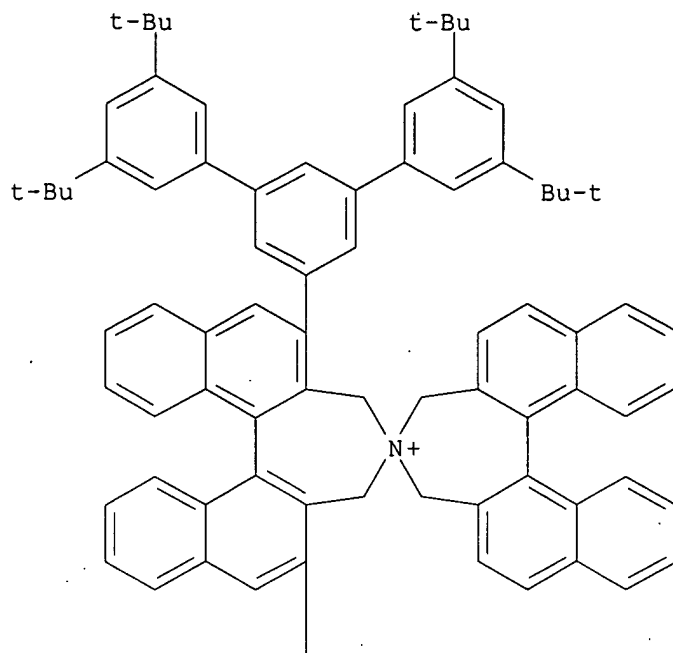
CN 4,4'-Spiro[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(1,1-dimethylethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide (1:1), (11bS,11'bs)-(CA INDEX NAME)



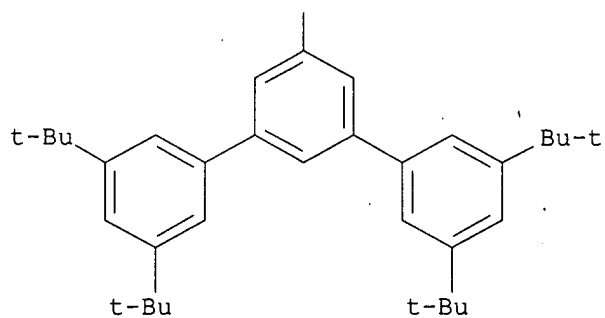
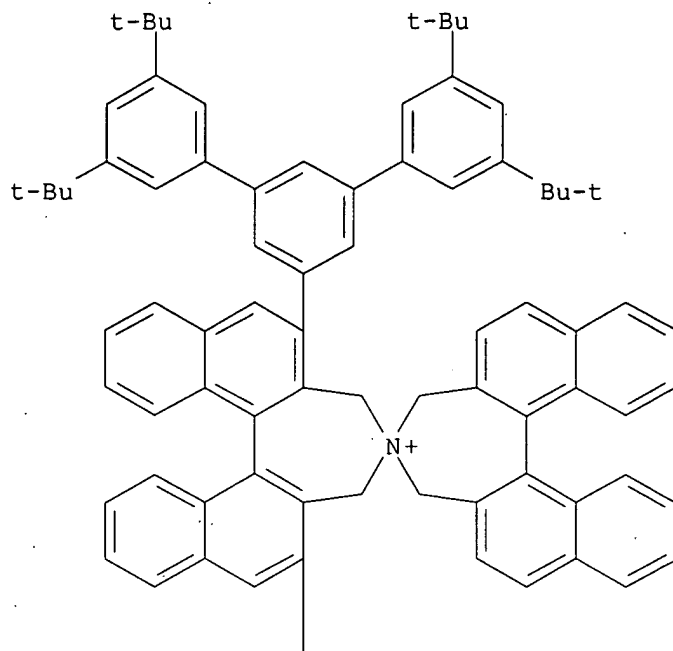
● Br<sup>-</sup>

RN 501934-21-0 CAPLUS

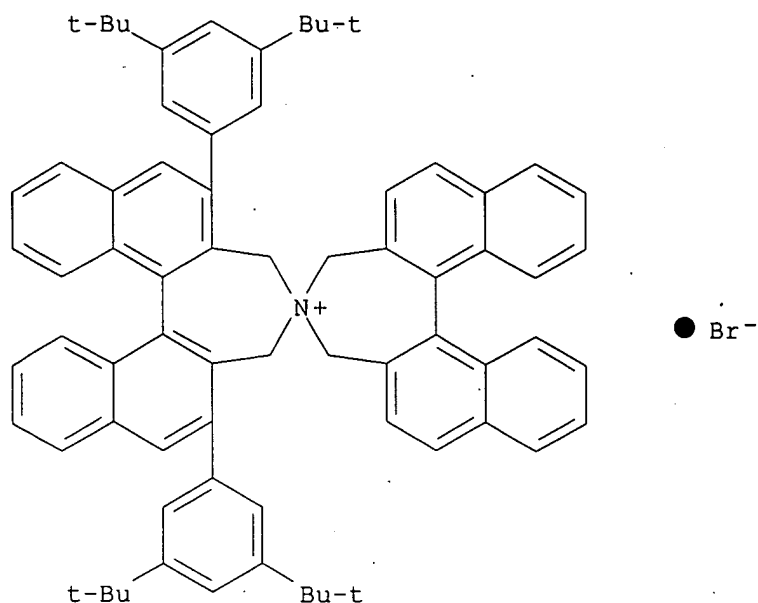
CN 4,4'-Spiro[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[3,3'',5,5''-tetrakis(1,1-dimethylethyl)[1,1':3',1''-terphenyl]-5'-yl]-, bromide (1:1), (11bS,11'bs)-(CA INDEX NAME)



RN 534576-68-6 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
 2,6-bis[3,3',5,5'-tetrakis(1,1-dimethylethyl)[1,1':3',1''-terphenyl]-5'-  
 yl]-, bromide, (11bR,11'bR)- (9CI) (CA INDEX NAME)



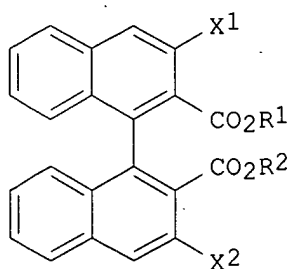
RN 724425-22-3 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(1,1-dimethylethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide, (11bR,11'bR)- (9CI)  
 (CA INDEX NAME)



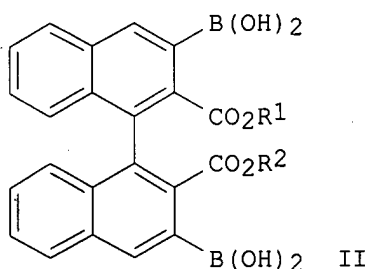
REFERENCE COUNT: 36 THERE ARE 36 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 46 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2004:351640 CAPLUS  
 DOCUMENT NUMBER: 140:357222  
 TITLE: Preparation of 3,3'-disubstituted 2,2'-bis(alkoxycarbonyl)-1,1'-binaphthyl and N-spiro quaternary ammonium salts having axial chirality for phase transfer catalysts  
 INVENTOR(S): Maruoka, Keiji  
 PATENT ASSIGNEE(S): Nagase Sangyo K. K., Japan  
 SOURCE: Jpn. Kokai Tokkyo Koho, 30 pp.  
 CODEN: JKXXAF  
 DOCUMENT TYPE: Patent  
 LANGUAGE: Japanese  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 2004131447	A	20040430	JP 2002-299317	20021011
PRIORITY APPLN. INFO.:			JP 2002-299317	20021011
OTHER SOURCE(S):		MARPAT 140:357222		
GI				



I



II



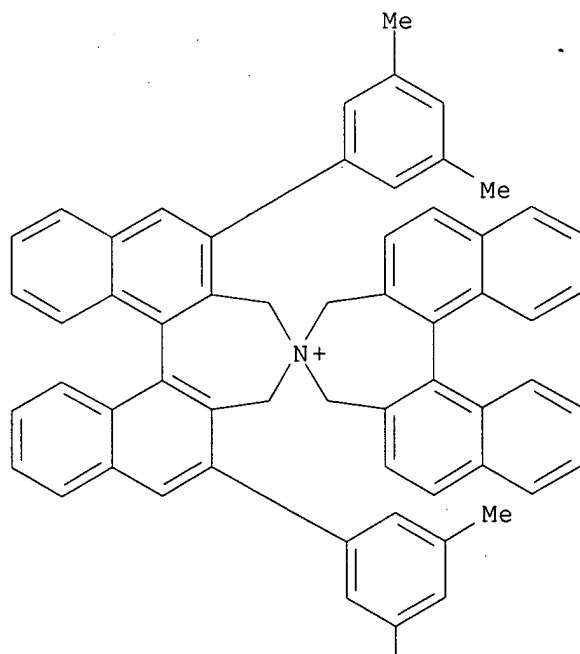
AB N-spiro quaternary ammonium salts, useful as phase transfer catalysts (no data), are prepared by reaction of binaphthyls I (X1, X2 = group reactive with boronic acids; R1, R2 = C1-4 alkyl) with  $\geq 1$  compds. selected from ArB(OH)<sub>2</sub> [Ar = C1-4 alkyl-, C1-4 alkoxy-, halo-, or aromatic hydrocarbyl-(un)substituted aryl, C1-4 alkyl-, C1-4 alkoxy-, halo-, or aromatic hydrocarbyl-(un)substituted heteroaryl, etc.], substitution of alkoxy-carbonyl groups in the resulting compds. with halogenomethyl groups, and reaction with (S)- or (R)-1,2-dihydro-7H-dinaphtho[2,1-c:1',2'-e]azepine. N-spiro quaternary ammonium salts are also prepared from binaphthyls II (R1, R2 = C1-4 alkyl) with  $\geq 1$  compds. selected from ArX (Ar = same as above; X = iodide, Br, Cl, F3CSO<sub>3</sub>).

(S)-3,3'-dibromo-2,2'-bis(isopropoxycarbonyl)-1,1'-binaphthyl [prepared from (S)-2,2'-bis(isopropoxycarbonyl)-1,1'-binaphthyl] was reacted with 3,5-dimethylphenylboronic acid in the presence of palladium acetate, Ph<sub>3</sub>P, and NaHCO<sub>3</sub> in 1,2-Dimethoxyethane-H<sub>2</sub>O under reflux for 20 h, treated with LiAlH<sub>4</sub> in THF at room temperature for 4 h, and brominated with PBr<sub>3</sub> in THF at room temperature for 1 h to give (S)-2,2'-bis(dibromomethyl)-3,3'-bis(3,5-dimethylphenyl)-1,1'-binaphthyl, which was treated with (S)-1,2-dihydro-7H-dinaphtho[2,1-c:1',2'-e]azepine in the presence of K<sub>2</sub>CO<sub>3</sub> in acetonitrile under reflux for 6 h to give 96% corresponding N-spiro quaternary ammonium salt.

IT 561054-89-5P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (preparation of N-spiro quaternary ammonium salts by reaction of binaphthyls with boronic acids, halomethylation, and reaction with dihydrodinaphthoazepine)

RN 561054-89-5 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis(3,5-dimethylphenyl)-3,3',5,5'-tetrahydro-, bromide, (11bS,11'bS)- (9CI) (CA INDEX NAME)

PAGE 1-A

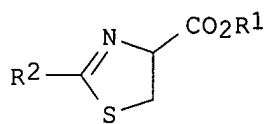


Me

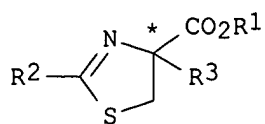
● Br<sup>-</sup>

L3 ANSWER 47 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2004:308425 CAPLUS  
 DOCUMENT NUMBER: 140:321719  
 TITLE: Process for producing optically active  
 $\alpha$ -substituted cysteine or salt thereof,  
 intermediate therefor, and process for producing the  
 same  
 INVENTOR(S): Maruoka, Keiji; Ooi, Takashi; Inoue, Kenji  
 PATENT ASSIGNEE(S): Kaneka Corporation, Japan  
 SOURCE: PCT Int. Appl., 36 pp.  
 CODEN: PIXXD2  
 DOCUMENT TYPE: Patent  
 LANGUAGE: Japanese  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

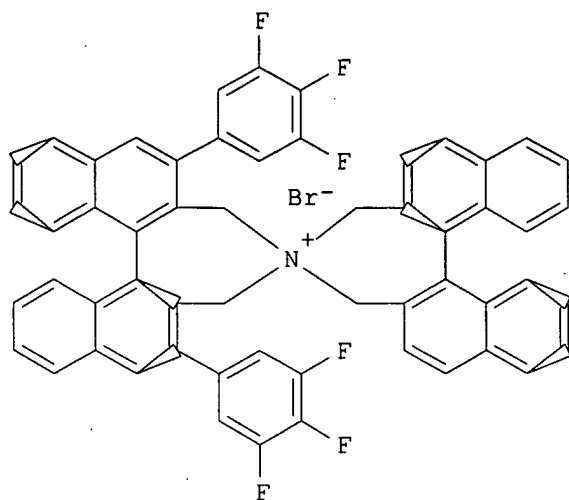
PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2004031163	A1	20040415	WO 2003-JP12565	20031001
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
AU 2003268706	A1	20040423	AU 2003-268706	20031001
EP 1548013	A1	20050629	EP 2003-748633	20031001
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, HU, SK				
US 20060069134	A1	20060330	US 2005-529039	20050324
PRIORITY APPLN. INFO.:			JP 2002-288401	A 20021001
			JP 2003-201787	A 20030725
			WO 2003-JP12565	W 20031001
OTHER SOURCE(S):		CASREACT 140:321719; MARPAT 140:321719		
GI				



I



II



I

AB Disclosed is a practical process for easily or industrially advantageously producing from an easily available inexpensive material an optically active  $\alpha$ -substituted cysteine or salt thereof useful as an intermediate for medicines, etc. The process, which is for producing an optically active  $\alpha$ -substituted cysteine of formula  $R^3C^*(NH_2)(CH_2SH)CO_2H$  [ $C^*$  = an asym. carbon atom;  $R^3$  = each (un)substituted linear, branched or cyclic C1-20 alkyl, linear, branched or cyclic C2-20 alkenyl, linear, branched or cyclic C2-20 alkynyl, linear, branched or cyclic C3-20 alkoxy carbonyl, C7-30 aralkyl, or C4-30 heteroaralkyl], comprise converting a cysteine derivative into a thiazoline compound [I;  $R^1$  = each (un)substituted linear, branched, or cyclic C1-10 alkyl or C1-10 alkylsilyl;  $R^2$  = each (un)substituted C6-30 aryl or linear, branched, or cyclic C1-20 alkyl], subjecting the compound I to a stereoselective substituent-introducing reaction with a compound  $R^3-L$  ( $R^3$  = same as above;  $L$  = a leaving group) in the presence of the aid of an optically active quaternary ammonium salt, especially an axially asym. quaternary ammonium salt, as a catalyst to thereby obtain an optically active thiazoline compound (II;  $R^1-R^3$  = same as above), and hydrolyzing the compound II. Thus, 2 mL toluene was added to 79.0 mg tert-Bu (R)-2-phenylthiazoline-4-carboxylate (III) (preparation given) and 2.74 mg an optically active quaternary ammonium salt [(S,S)-IV], treated with 37.3  $\mu$ L MeI, cooled to 0°, treated with 1 mL 50% aqueous KOH, and stirred until the compound III disappeared to give, m after workup and silica gel chromatog., 86% tert-Bu (R)-4-methyl-2-phenylthiazoline-4-carboxylate (V) (97% ee). The compound V (1 g) and 10 g 4 N aqueous HCl were added to glass vessel and refluxed until the compound V disappeared. The reaction mixture was concentrated to approx. 1/6 of the

original

volume under reduced pressure, codistd. with 5 mL toluene three times to give, after filtration of the precipitated crystals, washing with toluene, and drying under reduced pressure overnight, 88.0% (R)- $\alpha$ -methyl-L-cysteine hydrochloride.

IT 287384-12-7

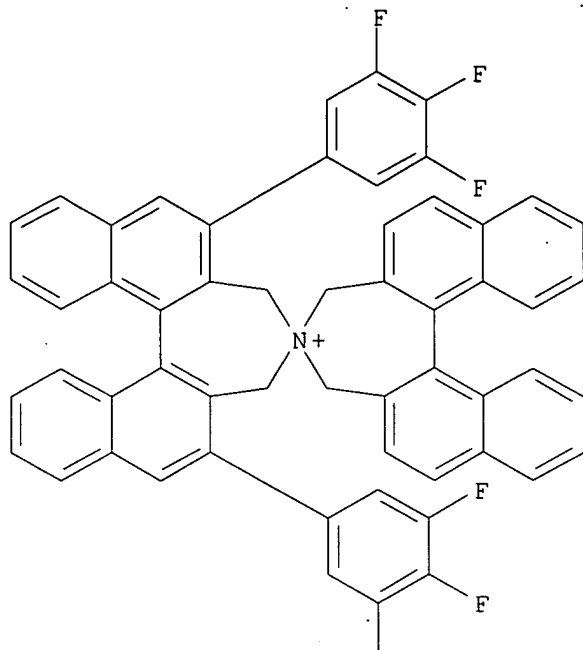
RL: CAT (Catalyst use); USES (Uses)

(process for producing optically active  $\alpha$ -substituted cysteine or salt thereof by stereoselective alkylation of thiazolinecarboxylic acid esters in presence of optically active quaternary ammonium salt)

RN 287384-12-7 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)

PAGE 1-A



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● Br<sup>-</sup>

REFERENCE COUNT: 10 THERE ARE 10 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 48 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2004:304173 CAPLUS

DOCUMENT NUMBER: 141:54590

TITLE: Design of new polyamine-based chiral phase-transfer catalysts for the enantioselective synthesis of phenylalanine

AUTHOR(S): Kano, Taichi; Konishi, Shunsuke; Shirakawa, Seiji; Maruoka, Keiji

CORPORATE SOURCE: Graduate School of Science, Department of Chemistry, Kyoto University, Sakyo, Kyoto, 606-8502, Japan

SOURCE: Tetrahedron: Asymmetry (2004), 15(8), 1243-1245

CODEN: TASYE3; ISSN: 0957-4166

PUBLISHER: Elsevier Science B.V.

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 141:54590

AB Enantiomerically enriched phenylalanine was synthesized by asym.

benzylation of a glycine Schiff base using polyamine-based chiral phase-transfer catalysts.

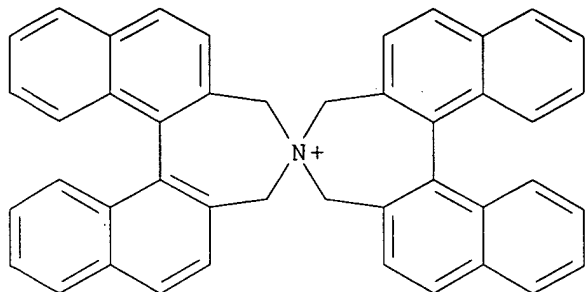
IT 237762-40-2

RL: CAT (Catalyst use); USES (Uses)

(preparation of binaphthyl chiral amines as phase-transfer catalysts for asym. benzylation of glycinate Schiff base)

RN 237762-40-2 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



● Br<sup>-</sup>

REFERENCE COUNT:

32

THERE ARE 32 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 49 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2004:99228 CAPLUS

DOCUMENT NUMBER: 140:304065

TITLE: Highly enantioselective alkylation of glycine methyl and ethyl ester derivatives under phase-transfer conditions: its synthetic advantage

AUTHOR(S): Ooi, Takashi; Uematsu, Yukitaka; Maruoka, Keiji  
CORPORATE SOURCE: Graduate School of Science, Department of Chemistry, Kyoto University, Sakyo, Kyoto, 606-8502, Japan

SOURCE: Tetrahedron Letters (2004), 45(8), 1675-1678

CODEN: TELEAY; ISSN: 0040-4039

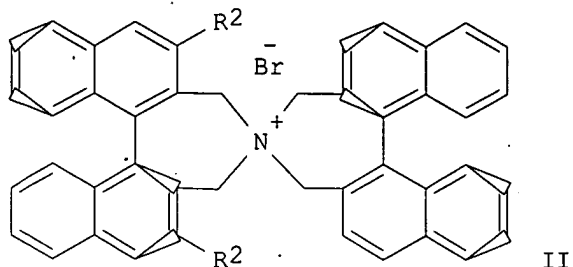
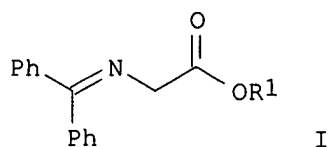
PUBLISHER: Elsevier Science B.V.

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 140:304065

GI



AB Phase-transfer alkylation of the benzophenone Schiff base of glycine Me or Et ester I (R1 = Me, Et) was found to be catalyzed by 3,4,5-F3-C6H2-NAS-Br [(S,S)-II] (R2 = 3,4,5-FC6H2) with high efficiency and excellent enantioselectivity. This procedure allows facile derivatization of the resulting alkylation products to other synthetically useful chiral building blocks.

IT 287384-12-7

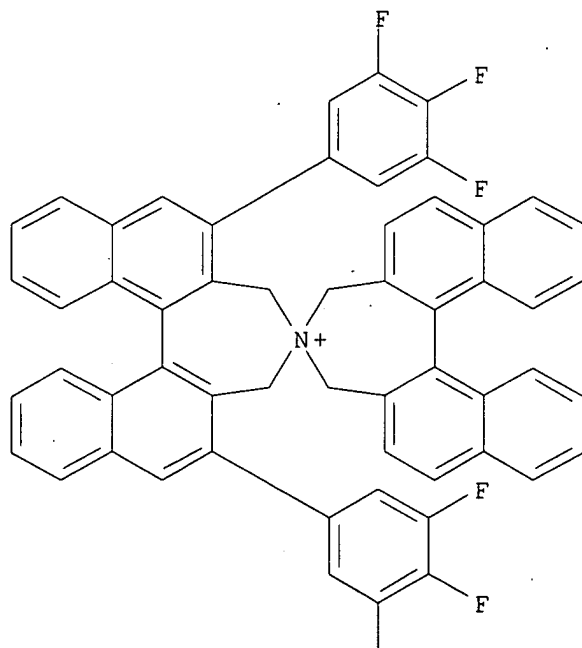
RL: CAT (Catalyst use); USES (Uses)

(phase-transfer asym. alkylation of benzophenone Schiff base of glycine Me or Et ester with chiral quaternary ammonium bromide as catalyst)

RN 287384-12-7 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)

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● Br<sup>-</sup>

REFERENCE COUNT: 30 THERE ARE 30 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 50 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2003:1008280 CAPLUS

DOCUMENT NUMBER: 140:181131

TITLE: Practical asymmetric synthesis of vicinal diamines through the catalytic highly enantioselective alkylation of glycine amide derivatives

AUTHOR(S): Ooi, Takashi; Sakai, Daiki; Takeuchi, Mifune; Tayama, Eiji; Maruoka, Keiji

CORPORATE SOURCE: Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo, Kyoto, 606-8502, Japan

SOURCE: Angewandte Chemie, International Edition (2003), 42(47), 5868-5870

CODEN: ACIEF5; ISSN: 1433-7851

PUBLISHER: Wiley-VCH Verlag GmbH & Co. KGaA

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 140:181131

AB Phase-transfer catalysis (PTC) by a designer chiral quaternary ammonium bromide facilitated the direct, highly enantioselective introduction of a wide variety of substituents including cycloalkyl side chains at the  $\alpha$  position of a prochiral glycine amide derivative. A general, practical procedure for the asym. synthesis of structurally diverse monosubstituted vicinal diamines is presented.

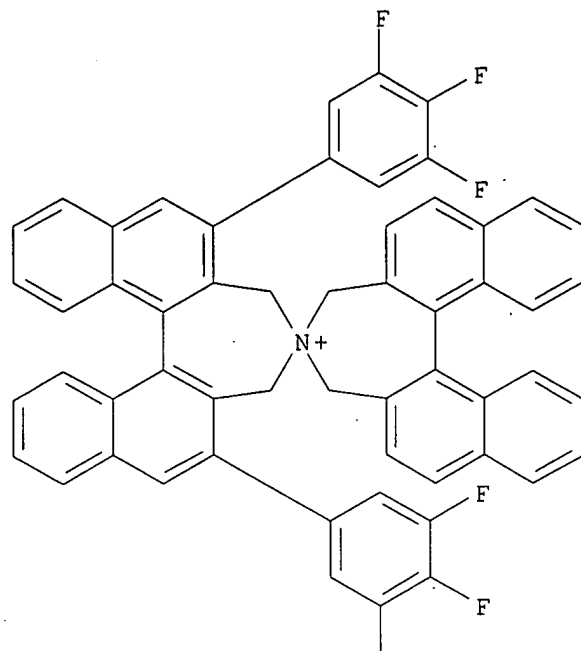
IT 287384-12-7 501934-20-9 501934-21-0

RL: CAT (Catalyst use); USES (Uses)

(stereoselective preparation of vicinal diamines via enantioselective phase-transfer alkylation of corresponding glycine amide derivs. catalyzed by chiral quaternary ammonium bromides)

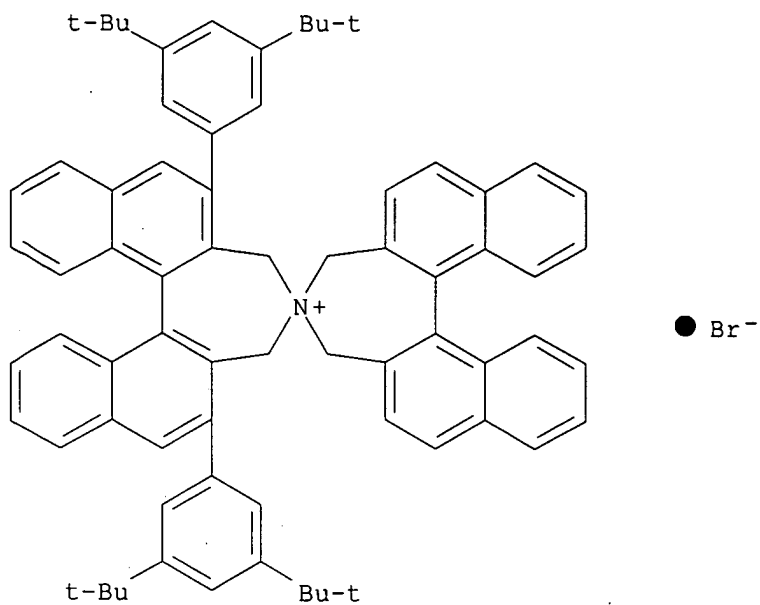
RN 287384-12-7 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bs)- (CA INDEX NAME)



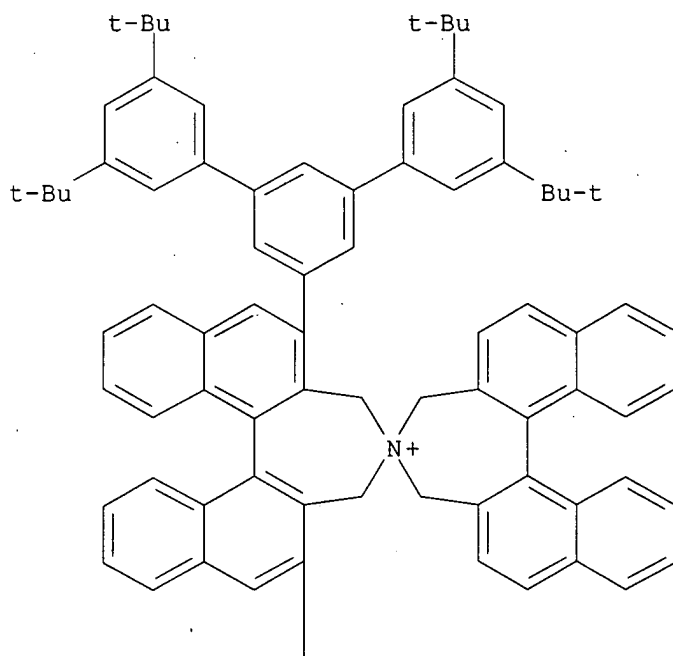
RN 501934-20-9 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(1,1-dimethylethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide (1:1), (11bS,11'bs)-  
 (CA INDEX NAME)

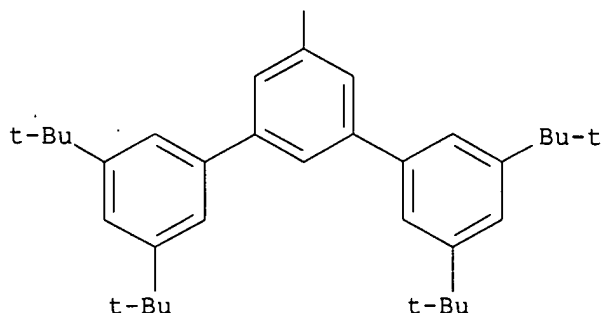




RN 501934-21-0 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[3,3'',5,5''-tetrakis(1,1-dimethylethyl)[1,1':3',1''-terphenyl]-5'-yl]-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)

PAGE 1-A





REFERENCE COUNT: 41 THERE ARE 41 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 51 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2003:910070 CAPLUS

DOCUMENT NUMBER: 140:339582

TITLE: Catalytic asymmetric synthesis of  $\alpha$ -amino acid derivatives and peptides using chiral phase-transfer catalysts

AUTHOR(S): Maruoka, Keiji

CORPORATE SOURCE: Department of Chemistry, Graduate School of Science, Kyoto University, Oiwake-cho, Kitashirakawa, Sakyo-ku, Kyoto, 606-8502, Japan

SOURCE: Proceedings of the Japan Academy, Series B: Physical and Biological Sciences (2003), 79(7), 181-189  
CODEN: PJABDW; ISSN: 0386-2208

PUBLISHER: Nippon Gakushuin

DOCUMENT TYPE: Journal; General Review

LANGUAGE: English

AB A review. The use of chiral binaphthyl phase-transfer catalysts for the stereoselective alkylation of amino acids was reviewed. Structurally rigid, chiral spiro ammonium salts of type (R, R)- or (S, S)-1 derived from com. available (R)- or (S)-1,1'-bi-2-naphthol have been designed as new C2-sym. chiral phase transfer catalysts and successfully applied to the highly efficient, catalytic enantioselective alkylation of tert-Bu glycinate Schiff base under mild phase transfer conditions to furnish  $\alpha$ -alkyl- $\alpha$ -amino acids and  $\alpha$ ,  $\alpha$ -dialkyl- $\alpha$ -amino acids with excellent enantioselectivity. These catalysts have been also utilized for the asym. terminal functionalization of peptides and asym. direct aldol reaction of glycine derivative

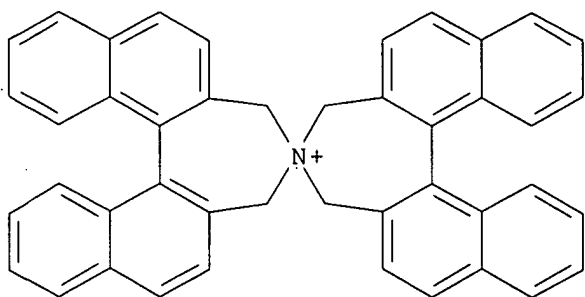
IT 237762-40-2D, derivs.

RL: CAT (Catalyst use); USES (Uses)

(use of binaphthyl chiral phase-transfer catalysts for stereoselective alkylation of amino acids)

RN 237762-40-2 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



● Br<sup>-</sup>

REFERENCE COUNT: 35 THERE ARE 35 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 52 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2003:902361 CAPLUS  
 DOCUMENT NUMBER: 139:381745  
 TITLE: Diastereoselective and enantioselective preparation of  $\beta$ -hydroxyamino acid esters using axially asymmetric N-spiroquaternary ammonium salts  
 INVENTOR(S): Maruoka, Keiji; Oi, Takashi  
 PATENT ASSIGNEE(S): Nagase and Co., Ltd., Japan  
 SOURCE: Jpn. Kokai Tokkyo Koho, 20 pp.  
 CODEN: JKXXAF  
 DOCUMENT TYPE: Patent  
 LANGUAGE: Japanese  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 2003327566	A	20031119	JP 2003-56980	20030304
PRIORITY APPLN. INFO.:			JP 2002-63184	A 20020308
OTHER SOURCE(S):	MARPAT 139:381745			
GI				

\* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT \*

AB HOCHR7CR3(NH2)CO2R4 [R3 = H, C1-6 (cyclo)alkyl, C2-6 (cyclo)alkenyl, C2-6 (cyclo)alkynyl, C6-10 aryl which may be substituted with C1-4 alkyl, C1-4 alkoxy, C2-4 alkenyl, C2-4 alkynyl, or halo, C1-6 heteroaryl which may be substituted with C1-4 alkyl, C2-6 alkynyl, or halo; R4 = C1-6 (cyclo)alkyl; R7 = H, C1-8 (cyclo)alkyl, C2-8 (cyclo)alkenyl, C6-10 aryl which may be substituted with C1-4 alkyl, halo, OH, or NO2, C1-9 heteroaryl which may be substituted with C1-4 alkyl, halo, OH, or NO2, C7-12 aralkyl], useful as chiral building blocks, are prepared by (1) treating R1R2C:NHR3CO2R4 (R1, R2 H, aryl which may be substituted with C1-4 alkyl, C1-4 alkoxy, C2-4 alkenyl, C2-4 alkynyl, or halo; R1 and/or R2 = group other than H; R3, R4 = same as above) with R7CHO (R7 = same as above) in a two-phase solvent system containing organic solvents and H2O in the presence of quaternary ammonium salts I [R5, R6 = H, C1-6 (halo)alkyl, C2-6 (halo)alkenyl, C2-6 (halo)alkynyl, (un)substituted aralkyl, (un)substituted heteroaralkyl, (un)substituted aryl, C1-3 alkoxy-carbonyl, N-C1-4 alkylcarbamoyl; Ar1, Ar2 = (un)substituted aryl, heteroaryl (substituents are given); X- = halo, SCN-, HSO4-; Y, Z = H, halo, C1-4

alkyl, C1-3 alkoxy; Y and Z may bonded together to represent direct bond] and (2) hydrolyzing the resulting Schiff bases. PhCH<sub>2</sub>CH<sub>2</sub>CHO was added dropwise to a mixture of a toluene solution of Ph<sub>2</sub>C:NCH<sub>2</sub>CO<sub>2</sub>CMe<sub>3</sub> and (S,S)-II, and an aqueous NaOH solution at 0° and the reaction mixture was further stirred at 0° for 2 h to give 80% PhCH<sub>2</sub>CH<sub>2</sub>CH(OH)CH(NH<sub>2</sub>)CO<sub>2</sub>CMe<sub>3</sub> with erythro (anti)/threo (syn) ratio 73:27.

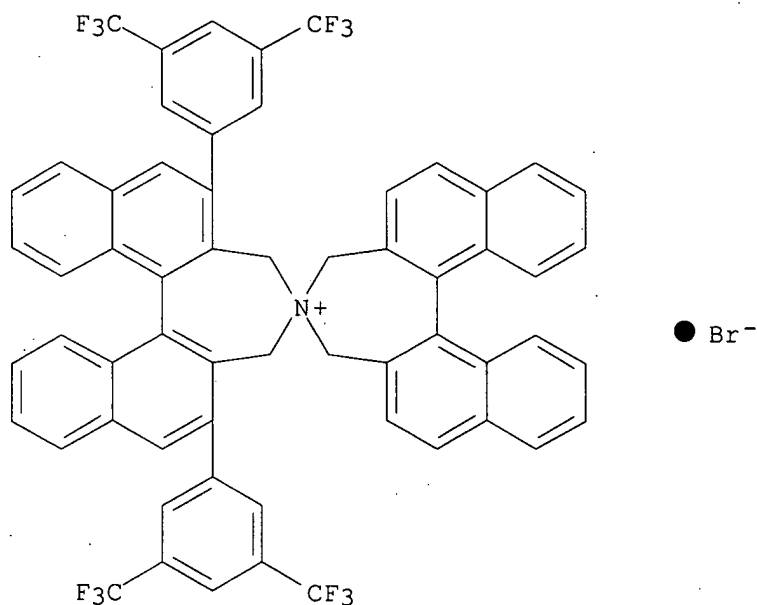
IT 438002-03-0 515137-97-0

RL: CAT (Catalyst use); USES (Uses)

(diastereoselective and enantioselective preparation of β-hydroxyamino acid esters from Schiff bases of amino acid esters and aldehydes using axially asym. N-spiroquaternary ammonium salts)

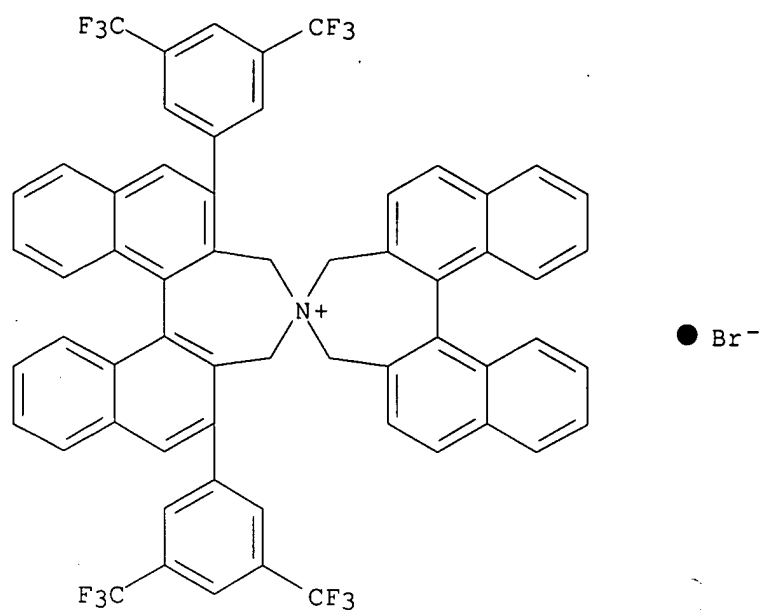
RN 438002-03-0 CAPLUS

CN 8,8'-Spirobi[8H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



RN 515137-97-0 CAPLUS

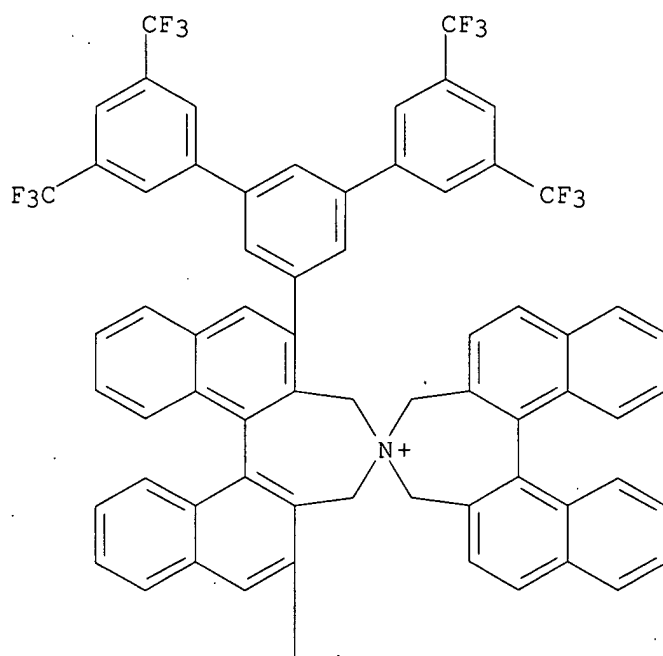
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide (1:1), (11bR,11'bR)- (CA INDEX NAME)

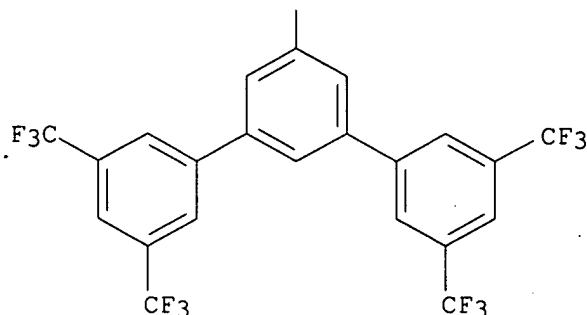


IT 515137-98-1P  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
 USES (Uses)  
 (diastereoselective and enantioselective preparation of  $\beta$ -hydroxyamino  
 acid esters from Schiff bases of amino acid esters and aldehydes using  
 axially asym. N-spiroquaternary ammonium salts)

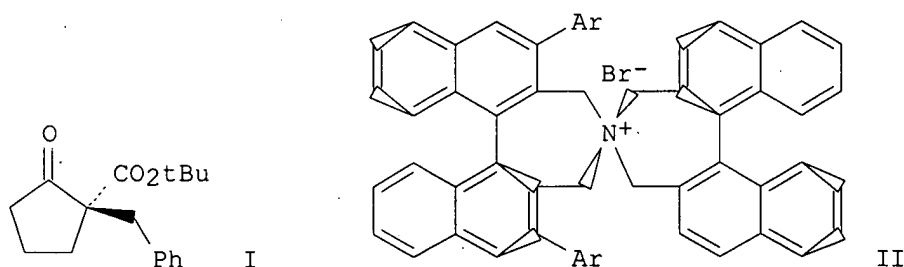
RN 515137-98-1 CAPLUS  
 CN 4,4'-Spiro[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
 2,6-bis[3,3'',5,5''-tetrakis(trifluoromethyl)[1,1':3',1''-terphenyl]-5'-  
 yl]-, bromide, (11bR,11'bR)- (9CI) (CA INDEX NAME)

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L3 ANSWER 53 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2003:709631 CAPLUS  
 DOCUMENT NUMBER: 139:350529  
 TITLE: Highly enantioselective construction of quaternary stereocenters on  $\beta$ -keto esters by phase-transfer catalytic asymmetric alkylation and Michael reaction  
 AUTHOR(S): Ooi, Takashi; Miki, Takashi; Taniguchi, Mika; Shiraishi, Misato; Takeuchi, Mifune; Maruoka, Keiji  
 CORPORATE SOURCE: Department of Chemistry, Kyoto University, Sakyo, Kyoto, 606-8502, Japan  
 SOURCE: Angewandte Chemie, International Edition (2003), 42(32), 3796-3798  
 CODEN: ACIEF5; ISSN: 1433-7851  
 PUBLISHER: Wiley-VCH Verlag GmbH & Co. KGaA  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 OTHER SOURCE(S): CASREACT 139:350529  
 GI



AB A phase-transfer-catalyzed asym. alkylation of  $\beta$ -keto esters to form alkyl keto esters, e.g., I, containing quaternary stereocenters, in high yields and enantioselectivities, is reported. The alkylation reaction requires a catalytic amount of chiral ammonium salt, II [Ar = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>] to obtain high enantioselectivity. This methodol. was applied to the Michael addition, which resulted in adducts containing quaternary

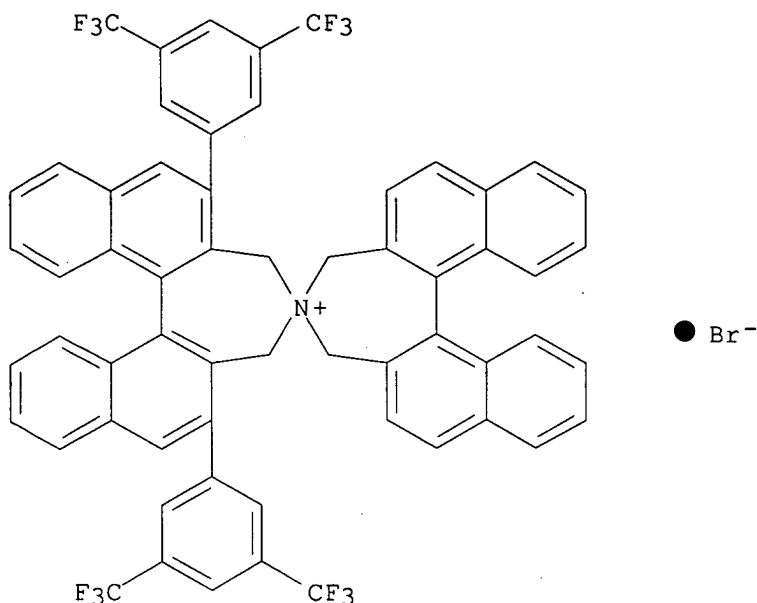
centers, with high enantioselectivities.

IT 438002-03-0

RL: CAT (Catalyst use); USES (Uses)

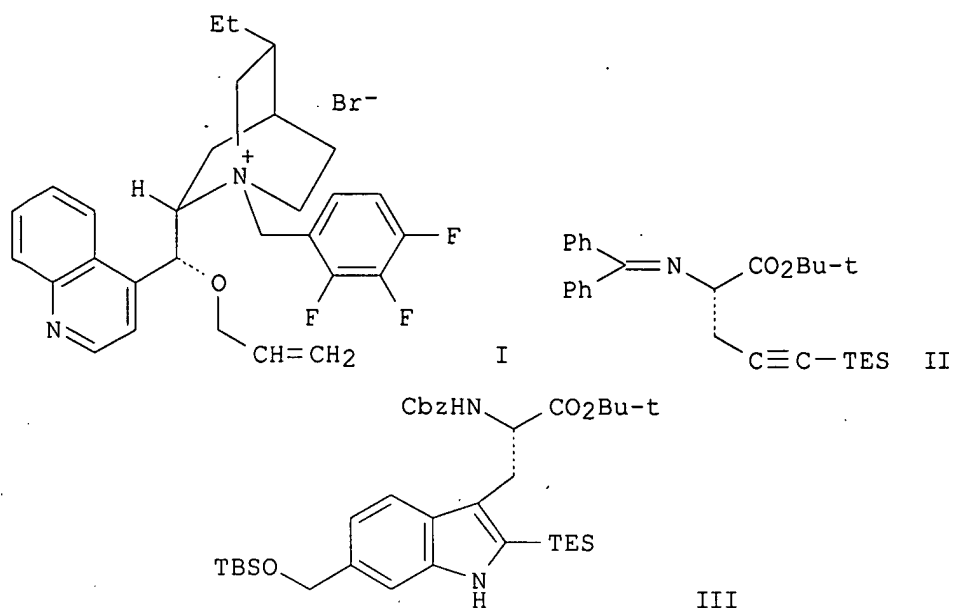
(stereoselective preparation of  $\alpha$ -alkyl  $\beta$ -keto esters via phase-transfer-catalyzed asym. alkylation of  $\beta$ -keto esters with

di-Me sulfate or alkyl bromides)  
 RN 438002-03-0 CAPLUS  
 CN 8,8'-Spirobi[8H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide (1:1), (11bS,11'bs)- (CA INDEX NAME)



REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 54 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2003:679488 CAPLUS  
 DOCUMENT NUMBER: 139:323759  
 TITLE: Catalytic Asymmetric Synthesis of the Central Tryptophan Residue of Celogentin C  
 AUTHOR(S): Castle, Steven L.; Srikanth, G. S. C.  
 CORPORATE SOURCE: Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT, 84602, USA  
 SOURCE: Organic Letters (2003), 5(20), 3611-3614  
 CODEN: ORLEF7; ISSN: 1523-7060  
 PUBLISHER: American Chemical Society  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 OTHER SOURCE(S): CASREACT 139:323759  
 GI

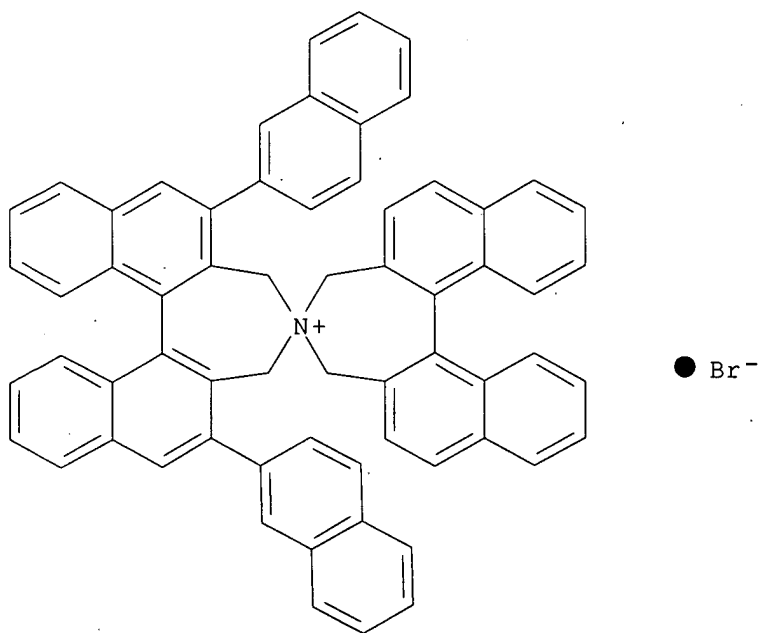


AB Chiral phase-transfer catalyst I containing an electron-deficient trifluorobenzyl moiety promoted the alkylation of glycinate  $\text{Ph}_2\text{C}:\text{NCH}_2\text{CO}_2\text{Bu-t}$  with propargyl bromide  $\text{BrCH}_2\text{C.tplbond.CTES}$  ( $\text{TES} = \text{SiEt}_3$ ) in good yield and excellent enantiomeric excess. The resulting propargyl glycine II was converted into tryptophan derivative III ( $\text{TBS} = \text{SiMe}_2\text{Bu-t}$ ) in two steps, with the Pd-catalyzed heteroannulation as the key transformation. This method promises to be an efficient route for the preparation of tryptophan derivs. possessing substitution on the indole ring.

IT 466679-91-4  
 RL: CAT (Catalyst use); USES (Uses)  
 (preparation of Trp residue of celogentin C by using chiral phase transfer catalysts for asym. alkylation of a glycinate derivative)

RN 466679-91-4 CAPLUS

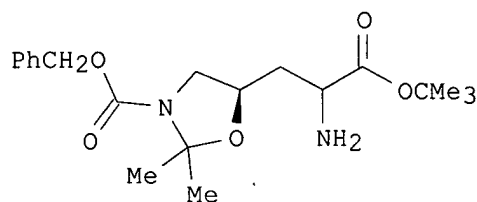
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-di-2-naphthalenyl-, bromide, (11bR,11'bR)- (9CI) (CA INDEX NAME)





REFERENCE COUNT: 29 THERE ARE 29 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

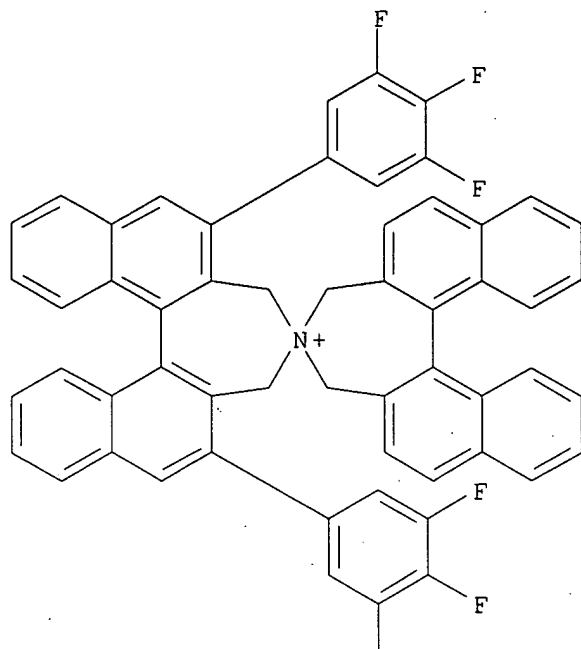
L3 ANSWER 55 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
ACCESSION NUMBER: 2003:657544 CAPLUS  
DOCUMENT NUMBER: 140:16939  
TITLE: Asymmetric synthesis of orthogonally protected  
(2S,4R)- and (2S,4S)-4-hydroxyornithine  
AUTHOR(S): Lepine, Renaud; Carbonnelle, Anny-Claude; Zhu, Jieping  
CORPORATE SOURCE: Institut de Chimie des Substances Naturelles, CNRS,  
Gif-sur-Yvette, 91198, Fr.  
SOURCE: Synlett (2003), (10), 1455-1458  
CODEN: SYNLES; ISSN: 0936-5214  
PUBLISHER: Georg Thieme Verlag  
DOCUMENT TYPE: Journal  
LANGUAGE: English  
OTHER SOURCE(S): CASREACT 140:16939  
GI



AB Synthesis of orthogonally protected (2S,4R)- and (2S,4S)-4-hydroxyornithines I is reported featuring an asym. alkylation of N-(diphenylmethylene)glycine tert-Bu ester with (5S)-N-benzyloxycarbonyl-5-iodomethyl oxazolidine. Double stereoselection was examined using chiral ammonium salts as phase transfer catalysts, and a substrate-directed chiral induction is documented.

IT 534570-50-8  
RL: CAT (Catalyst use); USES (Uses)  
(asym. synthesis of orthogonally protected hydroxyornithines and their derivs.)

RN 534570-50-8 CAPLUS  
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bR,11'bR)- (CA INDEX NAME)

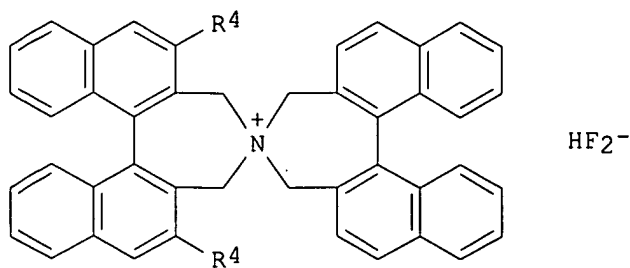


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● Br<sup>-</sup>

REFERENCE COUNT: 42 THERE ARE 42 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 56 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2003:509038 CAPLUS  
 DOCUMENT NUMBER: 139:197011  
 TITLE: Highly Enantioselective Michael Addition of Silyl Nitronates to  $\alpha,\beta$ -Unsaturated Aldehydes Catalyzed by Designer Chiral Ammonium Bifluorides: Efficient Access to Optically Active  $\gamma$ -Nitro Aldehydes and Their Enol Silyl Ethers  
 AUTHOR(S): Ooi, Takashi; Doda, Kanae; Maruoka, Keiji  
 CORPORATE SOURCE: Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto, 606-8502, Japan  
 SOURCE: Journal of the American Chemical Society (2003), 125(30), 9022-9023  
 CODEN: JACSAT; ISSN: 0002-7863  
 PUBLISHER: American Chemical Society  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 OTHER SOURCE(S): CASREACT 139:197011  
 GI



AB Highly enantioselective Michael addition of silyl nitronates  $R_1CH:N^+(O^-)OSiMe_3$  (I) ( $R_1 = Me, Et$ ) to  $\alpha,\beta$ -unsatd. aldehydes  $R_2CH:CR_3CHO$  [ $R_2 = Pr, Ph, R_3 = H, Me; R_2R_3 = (CH_2)_4$ ] in the presence of designer N-spiro C2-sym. chiral quaternary ammonium bifluoride II [ $R_4 = 3,5-(Me_3C)_2C_6H_3$ ] as a catalyst provided direct access to both optically active  $\gamma$ -nitro aldehydes  $R_1CH(NO_2)CHR_2CHR_3CHO$ , which are very useful precursors to various complex organic mols. including aminocarbonyls, and their enol silyl ethers  $R_1CH(NO_2)CHR_2CR_3:CHOSiMe_3$ . For instance, the reaction of I ( $R_1 = Me$ ) with trans-cinnamaldehyde in toluene in the presence of (R,R)-II (2 mol %) proceeded smoothly at  $-78^\circ$  to give the desired enol silyl ether  $MeCH(NO_2)CHPhCH:CHOSiMe_3$  (III) in 90% isolated yield (anti/syn = 83:17) with 97% ee (anti isomer), and simple treatment of III thus obtained with 1N HCl in THF at  $0^\circ$  afforded the corresponding  $\gamma$ -nitro aldehyde  $MeCH(NO_2)CHPhCH_2CHO$  quant. without loss of diastereo- and enantioselectivity.

IT 586344-86-7 586344-89-0

RL: CAT (Catalyst use); USES (Uses)

(asym. synthesis of  $\gamma$ -nitro aldehydes and their enol silyl ethers via Michael addition of silyl nitronates to  $\alpha,\beta$ -unsatd. aldehydes catalyzed by chiral ammonium bifluorides)

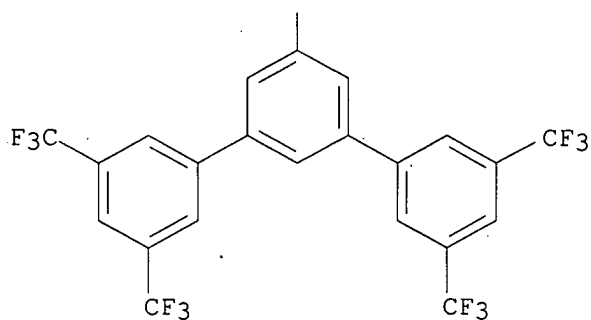
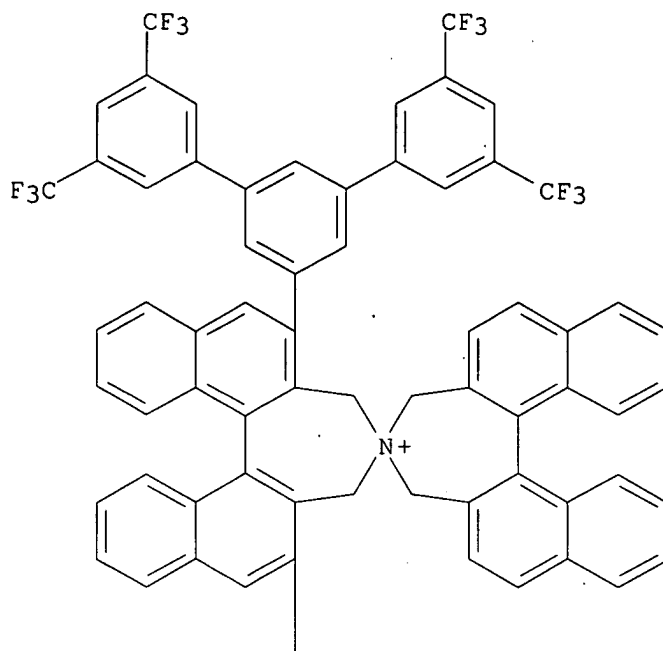
RN 586344-86-7 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[3,3'',5,5''-tetrakis(trifluoromethyl)[1,1':3',1''-terphenyl]-5'-yl]-, (11bR,11'bR)-, (hydrogen difluoride) (1:1) (CA INDEX NAME)

CM 1

CRN 586344-85-6

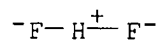
CMF C88 H48 F24 N



CM 2

CRN 18130-74-0

CMF F2 H



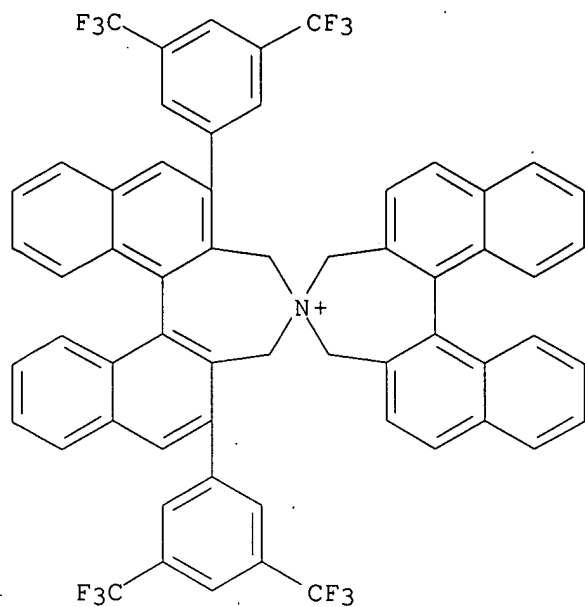
RN 586344-89-0 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, (11bR,11'bR)-, (hydrogen difluoride) (1:1) (CA INDEX NAME)

CM 1

CRN 586344-88-9

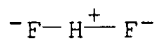
CMF C60 H36 F12 N



CM 2

CRN 18130-74-0

CMF F2 H



IT 586344-91-4P

RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
USES (Uses)

(asym. synthesis of  $\gamma$ -nitro aldehydes and their enol silyl ethers  
via Michael addition of silyl nitronates to  $\alpha,\beta$ -unsatd.  
aldehydes catalyzed by chiral ammonium bifluorides)

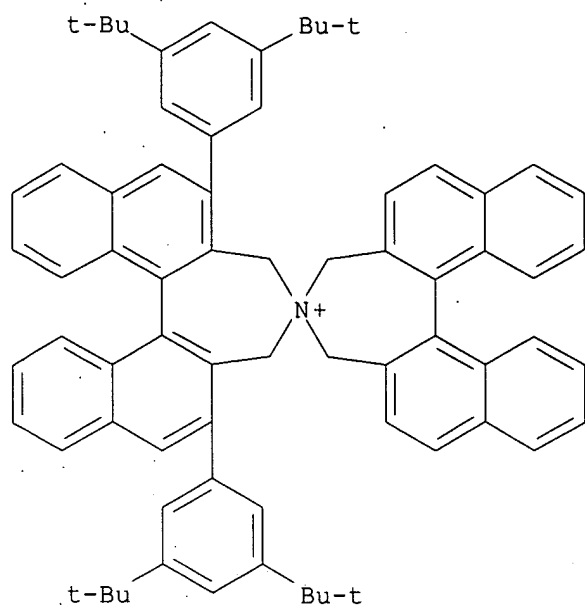
RN 586344-91-4 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(1,1-dimethylethyl)phenyl]-3,3',5,5'-tetrahydro-, (11bR,11'bR)-, (hydrogen difluoride) (1:1) (CA INDEX NAME)

CM 1

CRN 586344-90-3

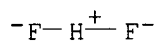
CMF C72 H72 N



CM 2

CRN 18130-74-0

CMF F2 H



REFERENCE COUNT: 25 THERE ARE 25 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 57 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2003:442711 CAPLUS

DOCUMENT NUMBER: 139:246185

TITLE: Symmetrical 4,4',6,6'-tetraarylbinaphthyl-substituted ammonium bromide as a new, chiral phase-transfer catalyst

AUTHOR(S): Hashimoto, Takuya; Tanaka, Youhei; Maruoka, Keiji

CORPORATE SOURCE: Graduate School of Science, Department of Chemistry, Kyoto University, Kyoto, 606-8502, Japan

SOURCE: Tetrahedron: Asymmetry (2003), 14(12), 1599-1602  
CODEN: TASYE3; ISSN: 0957-4166

PUBLISHER: Elsevier Science B.V.

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 139:246185

AB Binaphthyl-modified spiro-type sym. phase-transfer catalysts possessing 4,4',6,6'-tetraaryl substituents are shown to exhibit high asym. induction in asym. alkylation of benzophenone imine glycine tert-Bu ester under ordinary phase-transfer conditions.

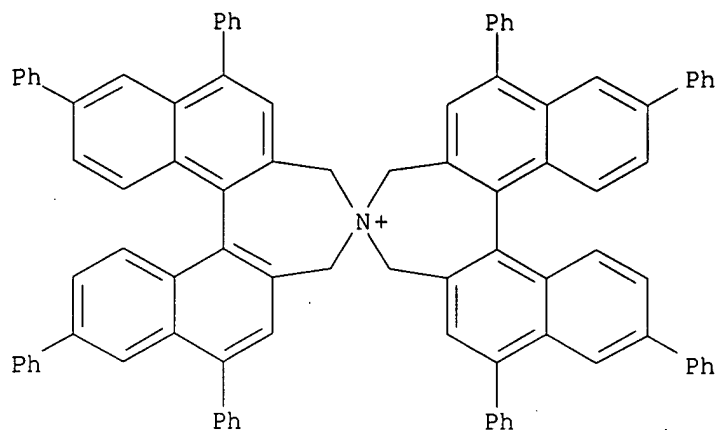
IT 596107-91-4P 596107-92-5P 596107-93-6P  
596107-94-7P

RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
USES (Uses)

(preparation of tetraarylbinaphthyl-substituted ammonium bromides as chiral phase-transfer catalysts and their using for asym. alkylation of benzophenone imine glycine tert-Bu ester)

RN 596107-91-4 CAPLUS

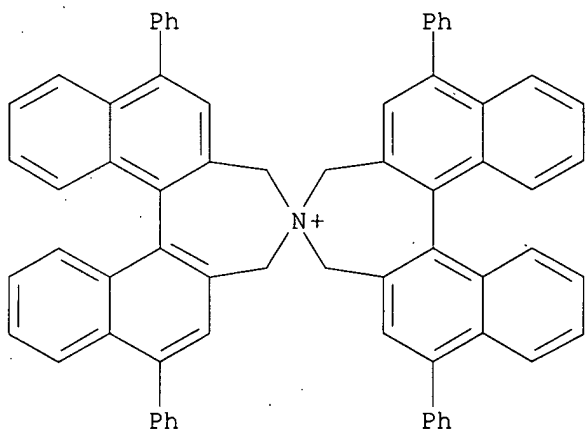
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-1,1',7,7',9,9',14,14'-octaphenyl-, bromide, (11bS,11'bs)- (9CI) (CA INDEX NAME)



● Br<sup>-</sup>

RN 596107-92-5 CAPLUS

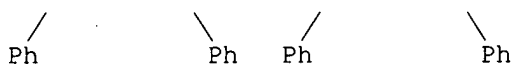
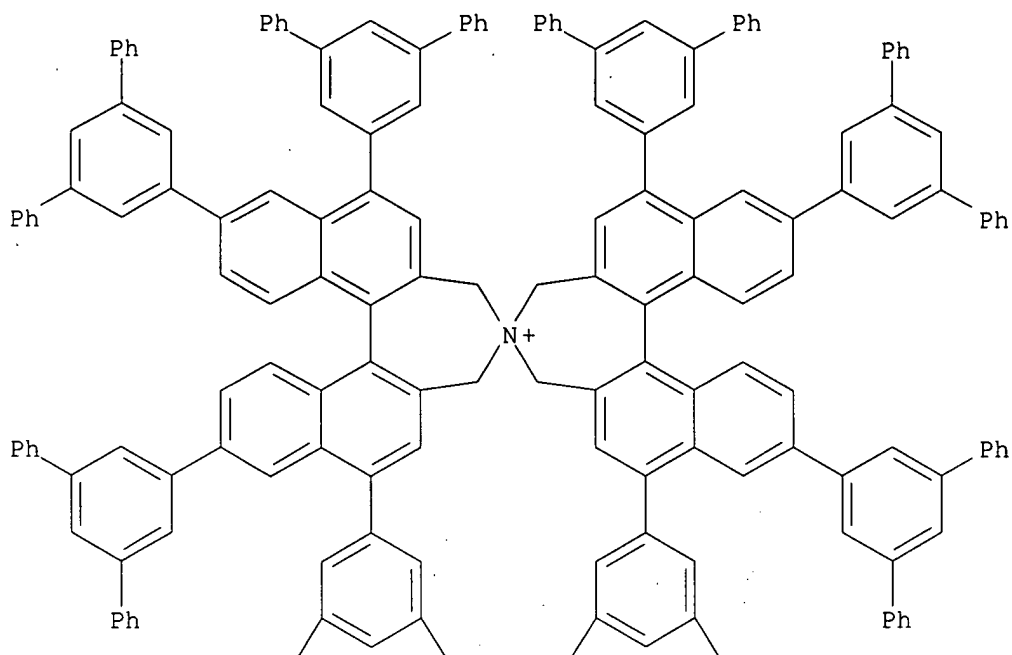
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-1,1',7,7'-tetraphenyl-, bromide, (11bS,11'bs)- (9CI) (CA INDEX NAME)



● Br<sup>-</sup>

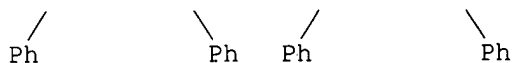
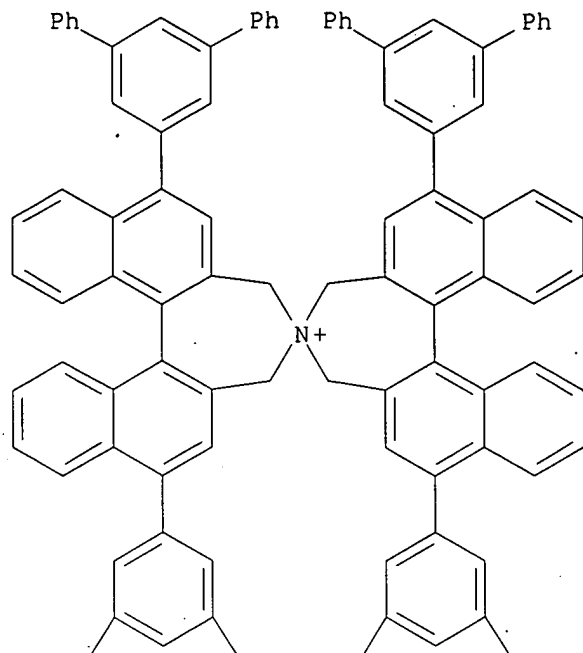
RN 596107-93-6 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-1,1',7,7',9,9',14,14'-octakis([1,1':3',1''-terphenyl]-5'-yl)-, bromide, (11bS,11'bs)- (9CI) (CA INDEX NAME)



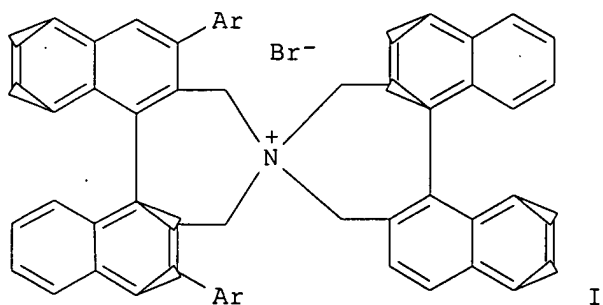
RN 596107-94-7 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
 1,1',7,7'-tetrakis([1,1':3',1''-terphenyl]-5'-yl)-, bromide, (11bS,11'bs)-  
 (9CI) (CA INDEX NAME)





REFERENCE COUNT: 21 THERE ARE 21 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 58 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2003:336128 CAPLUS  
 DOCUMENT NUMBER: 139:101015  
 TITLE: New, Improved Procedure for the Synthesis of Structurally Diverse N-Spiro C2-Symmetric Chiral Quaternary Ammonium Bromides  
 AUTHOR(S): Ooi, Takashi; Uematsu, Yukitaka; Maruoka, Keiji  
 CORPORATE SOURCE: Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto, 606-8502, Japan  
 SOURCE: Journal of Organic Chemistry (2003), 68(11), 4576-4578  
 CODEN: JOCEAH; ISSN: 0022-3263  
 PUBLISHER: American Chemical Society  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 OTHER SOURCE(S): CASREACT 139:101015  
 GI



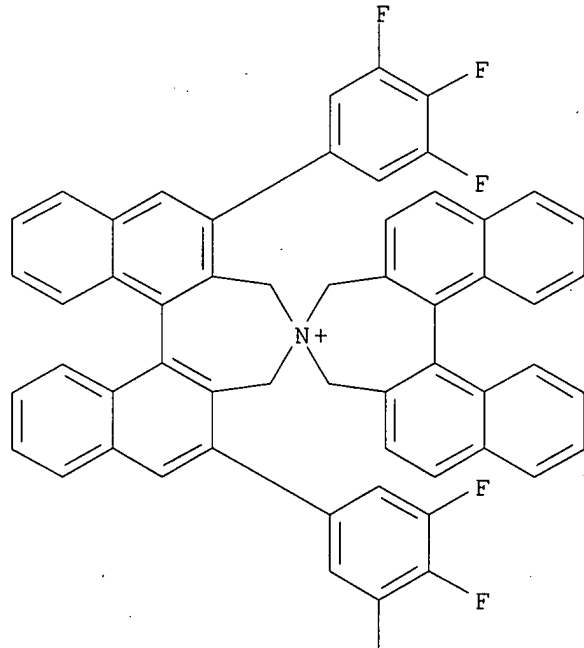
AB Selective, direct ortho magnesiation of (S)-2,2'-bis(isopropoxycarbonyl)-1,1'-binaphthyl has been achieved under mild conditions, using magnesium bis(2,2,6,6-tetramethylpiperamide) [Mg(TMP)2]. In combination with the subsequent reaction with the appropriate electrophiles, bromine and iodine, this method constitutes a key step in establishing a new and concise synthetic route to a wide variety of N-spiro C2-sym. chiral quaternary ammonium bromides of type I [Ar = 3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 3,4,5-F<sub>3</sub>C<sub>6</sub>H<sub>2</sub>].

IT 287384-12-7P 561054-89-5P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (preparation of bis(binaphthalenedimethyl)ammonium bromides)

RN 287384-12-7 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)

PAGE 1-A

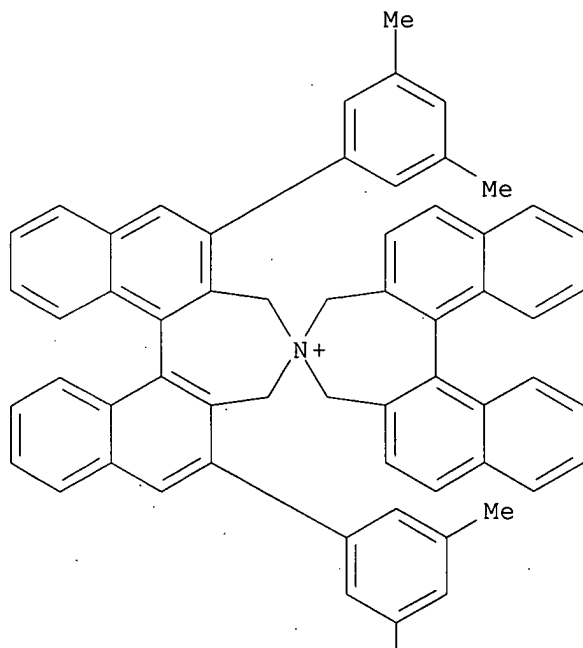


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F

● Br<sup>-</sup>

RN 561054-89-5 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis(3,5-dimethylphenyl)-3,3',5,5'-tetrahydro-, bromide, (11bS,11'bS)- (9CI) (CA INDEX NAME)

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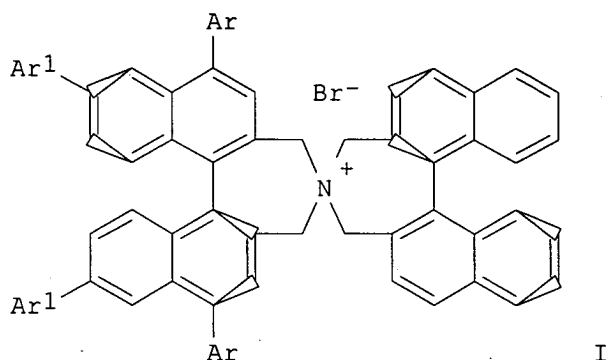
|  
Me

● Br<sup>-</sup>

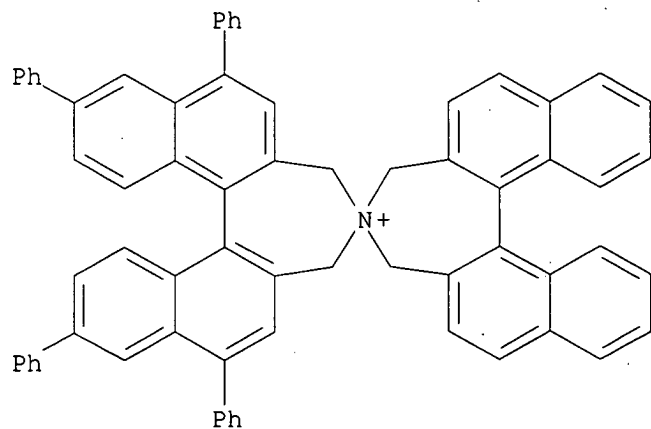
REFERENCE COUNT: 12 THERE ARE 12 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 59 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2003:262843 CAPLUS  
 DOCUMENT NUMBER: 139:197246  
 TITLE: Substituent effect of binaphthyl-modified spiro-type chiral phase-transfer catalysts  
 AUTHOR(S): Hashimoto, Takuya; Maruoka, Keiji  
 CORPORATE SOURCE: Graduate School of Science, Department of Chemistry,

SOURCE: Kyoto University, Kyoto, 606-8502, Japan  
 Tetrahedron Letters (2003), 44 (16), 3313-3316  
 CODEN: TELEAY; ISSN: 0040-4039  
 PUBLISHER: Elsevier Science Ltd.  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 OTHER SOURCE(S): CASREACT 139:197246  
 GI

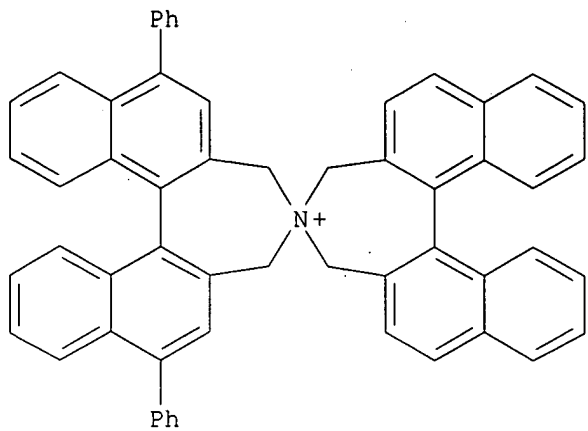


AB Binaphthyl-modified spiro-type phase-transfer catalysts possessing 4,4'-diaryl substituents are shown to exhibit high asym. induction in the benzylation of  $\text{Ph}_2\text{C:NCH}_2\text{CO}_2\text{Bu-t}$  under phase-transfer conditions. For example, spiro (diaryl)binaphthalene derivs. I-III ( $\text{Ar} = \text{Ar1} = \text{Ph}$ ;  $\text{Ar} = \text{Ph}$ ,  $\text{Ar1} = \text{H}$ ;  $\text{Ar} = \text{Ar1} = 3,5\text{-diphenylphenyl}$ ) were prepared and used as chiral catalysts for the asym. alkylation of  $\text{Ph}_2\text{C:NCH}_2\text{CO}_2\text{Bu-t}$  with  $\text{RBr}$  ( $\text{R} = \text{benzyl}$ , allyl, methallyl, propargyl, 4-fluorobenzyl, 1-naphthylmethyl).  
 IT 583050-09-3P 583050-10-6P 583050-11-7P  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
 USES (Uses)  
 (preparation of spiro binaphthyl derivs. as chiral phase-transfer catalysts for asym. alkylation of N-(diphenylmethylene)glycinate)  
 RN 583050-09-3 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-1,7,9,14-tetraphenyl-, bromide, (11bS,11'bs)- (9CI) (CA INDEX NAME)



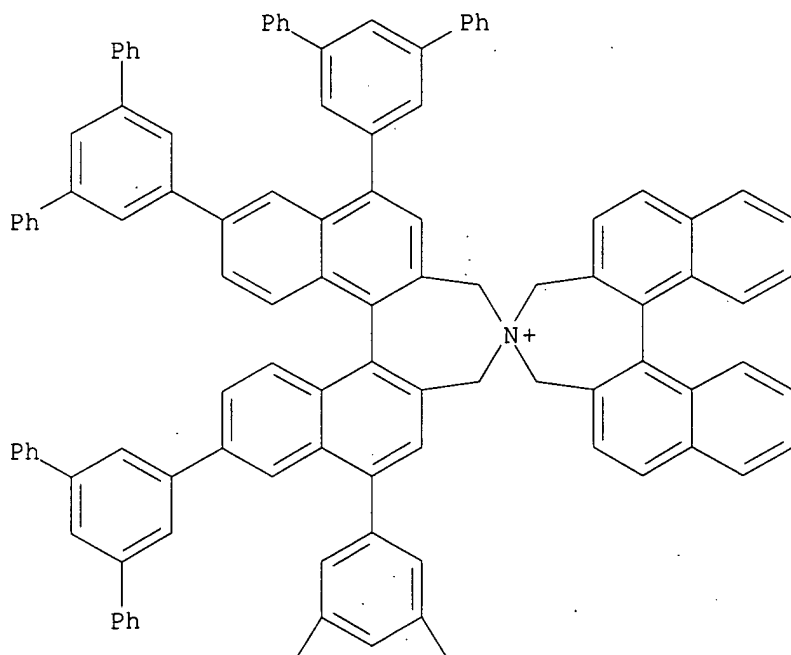
● Br<sup>-</sup>

RN 583050-10-6 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-1,7-diphenyl-, bromide, (11bS,11'bS)- (9CI) (CA INDEX NAME)



● Br<sup>-</sup>

RN 583050-11-7 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-1,7,9,14-tetrakis([1,1':3',1''-terphenyl]-5'-yl)-, bromide, (11bS,11'bS)- (9CI) (CA INDEX NAME)



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REFERENCE COUNT: 19 THERE ARE 19 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 60 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2003:251281 CAPLUS

DOCUMENT NUMBER: 139:7140

TITLE: Design of N-Spiro C2-Symmetric Chiral Quaternary Ammonium Bromides as Novel Chiral Phase-Transfer Catalysts: Synthesis and Application to Practical Asymmetric Synthesis of  $\alpha$ -Amino Acids

AUTHOR(S): Ooi, Takashi; Kameda, Minoru; Maruoka, Keiji

CORPORATE SOURCE: Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto, 606-8502, Japan

SOURCE: Journal of the American Chemical Society (2003), 125(17), 5139-5151

CODEN: JACSAT; ISSN: 0002-7863

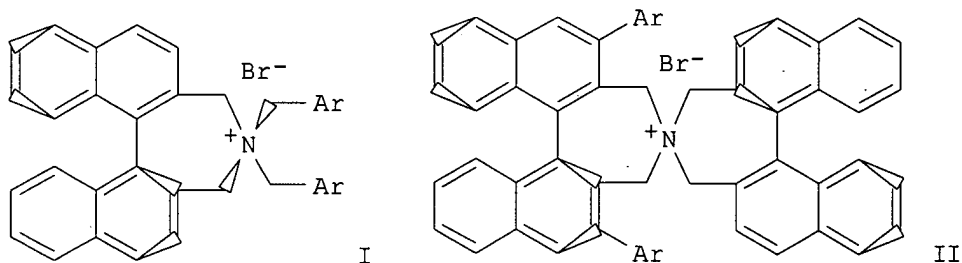
PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 139:7140

GI



AB Chiral phase-transfer catalysts, C2-sym. chiral quaternary ammonium bromides I (Ar = Ph,  $\alpha$ -naphthyl) and II [Ar = H, Ph,  $\beta$ -naphthyl, 3,5-(diphenyl)phenyl, 4-fluorophenyl, 3,4,5-trifluorophenyl], were readily prepared from com. available optically pure 1,1'-bi-2-naphthol. Detailed procedures for the synthesis of I and II were given, and the structures of II (Ar = H, 3,4,5-trifluorophenyl) were unequivocally determined by single-crystal x-ray diffraction anal. The reactivity and selectivity of these chiral ammonium bromides as chiral phase-transfer catalysts were evaluated in the asym. alkylation of  $\text{Ph}_2\text{C:NCH}_2\text{CO}_2\text{R}$  (R = Bu-t, Me,  $\text{CH}_2\text{Ph}$ ,  $\text{CHPh}_2$ ) by  $\text{PhCH}_2\text{Br}$  under mild liquid-liquid phase-transfer conditions, and the optimization of the reaction variables (solvent, base, and temperature) was conducted. In addition, the scope and limitations of this asym. alkylation were thoroughly investigated with a variety of alkyl halides, in which the advantage of the unique N-spiro structure of II and dramatic effect of the steric as well as the electronic properties of the aromatic substituents on the 3,3'-position of the binaphthyl moiety were emphasized. Finally, the asym. synthesis of Me and tert-Bu (S)-N-acetylindoline-2-carboxylates, and L-Dopa (L-3,4-dihydroxyphenylalanine) tert-Bu ester was successfully accomplished

using the above methodol.

IT 237762-40-2P 534570-52-0P

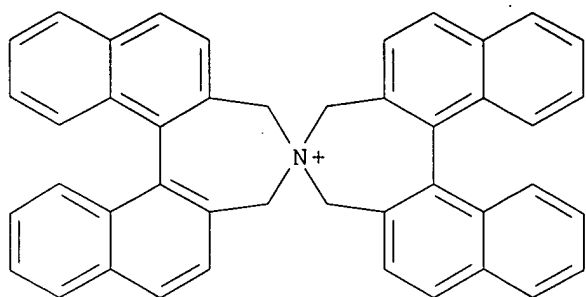
RL: CAT (Catalyst use); PRP (Properties); SPN (Synthetic preparation);

PREP (Preparation); USES (Uses)

(crystal structure; preparation of binaphthyl quaternary ammonium bromides as chiral phase-transfer catalysts for asym. alkylation of glycine Schiff base)

RN 237762-40-2 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



● Br<sup>-</sup>

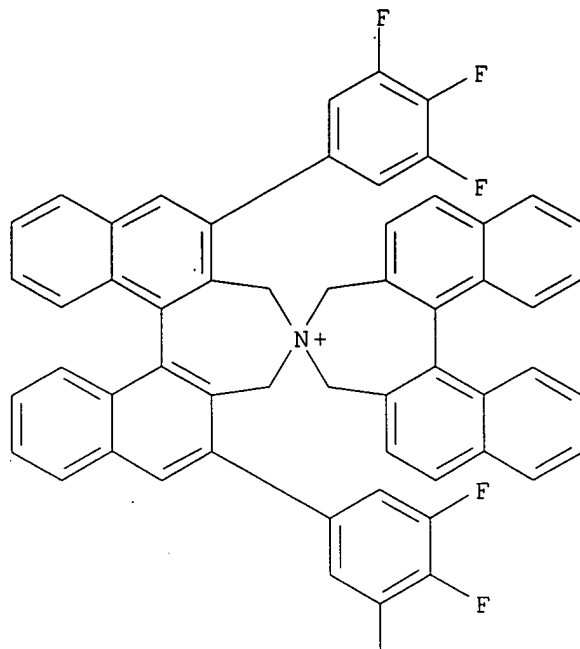
RN 534570-52-0 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, stereoisomer, hexafluorophosphate(1-) (9CI) (CA INDEX NAME)

CM 1

CRN 401846-45-5

CMF C56 H34 F6 N

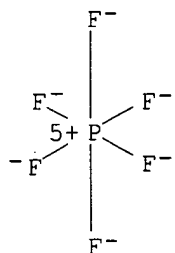


CM 2

CRN 16919-18-9

CMF F6 P

CCI CCS



IT 534570-50-8P

RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
USES (Uses)

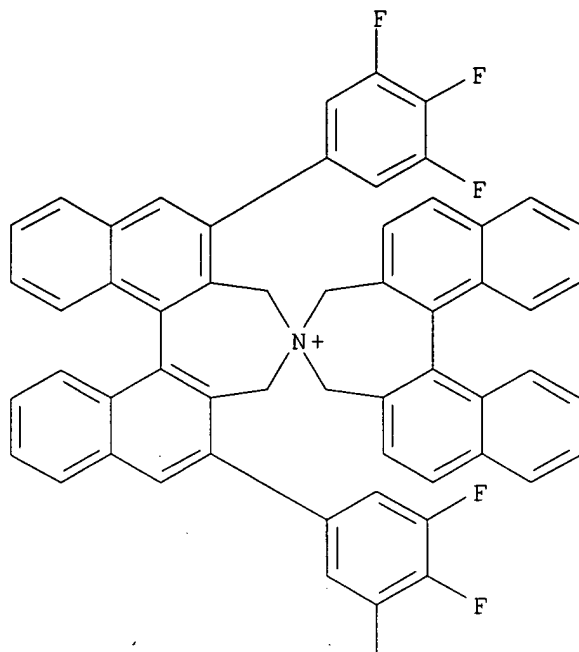
(preparation of amino acids by asym. alkylation of N-(diphenylmethylene)glycinate with alkyl bromides in presence of chiral quaternary ammonium bromide phase-transfer catalysts)

RN 534570-50-8 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bR,11'bR)- (CA INDEX NAME)



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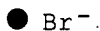
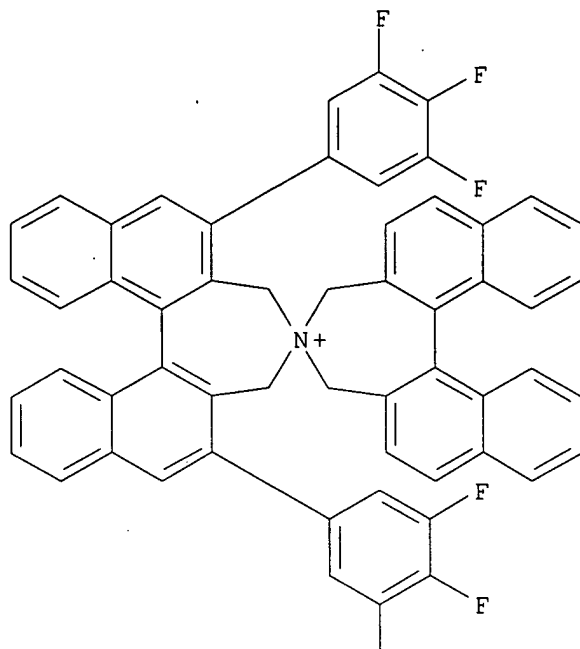


PAGE 2-A

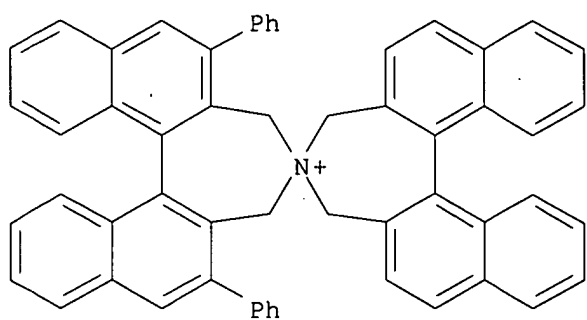
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● Br<sup>-</sup>

IT 287384-12-7P  
RL: CAT (Catalyst use); PRP (Properties); SPN (Synthetic preparation);  
PREP (Preparation); USES (Uses)  
(preparation of binaphthyl quaternary ammonium bromides as chiral  
phase-transfer catalysts for asym. alkylation of glycine Schiff base)  
RN 287384-12-7 CAPLUS  
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bS)- (CA INDEX  
NAME)

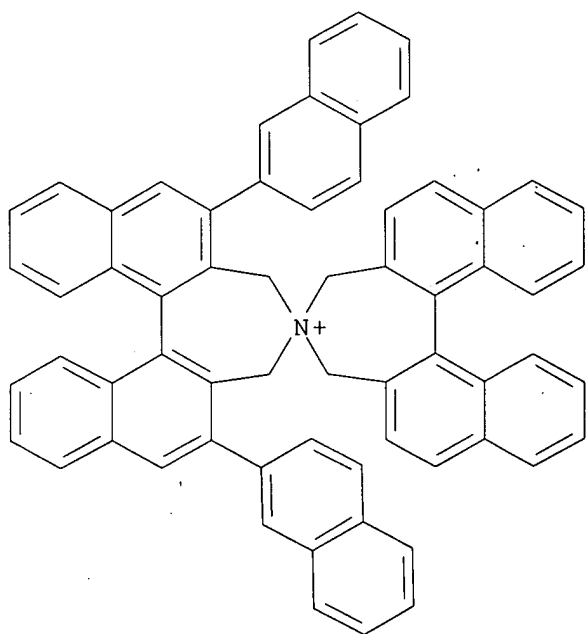


IT 237762-41-3P 237762-42-4P 534570-44-0P  
 534570-45-1P  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
 USES (Uses)  
 (preparation of binaphthyl quaternary ammonium bromides as chiral  
 phase-transfer catalysts for asym. alkylation of glycine Schiff base)  
 RN 237762-41-3 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
 2,6-diphenyl-, bromide, (11bS,11'bS)- (9CI) (CA INDEX NAME)



● Br<sup>-</sup>

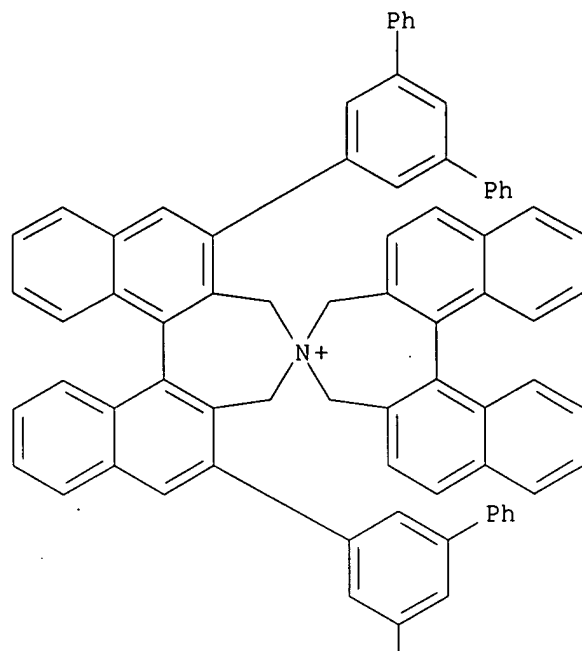
RN 237762-42-4 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-di-2-naphthalenyl-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



● Br<sup>-</sup>

RN 534570-44-0 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis([1,1':3',1''-terphenyl]-5'-yl)-3,3',5,5'-tetrahydro-, bromide, (11bS,11'bS)- (9CI) (CA INDEX NAME)

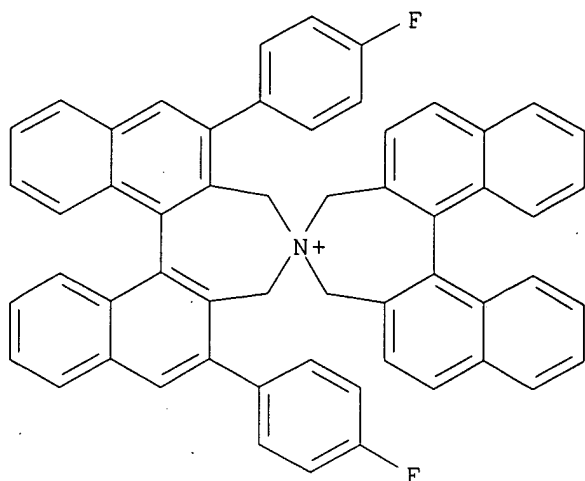
PAGE 1-A



PAGE 2-A



RN 534570-45-1 CAPLUS  
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis(4-fluorophenyl)-  
3,3',5,5'-tetrahydro-, bromide, (11bS,11'BS)- (9CI) (CA INDEX NAME)

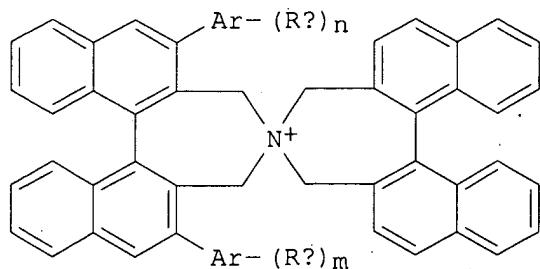


● Br<sup>-</sup>

REFERENCE COUNT: 10 THERE ARE 10 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 61 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2003:216947 CAPLUS  
 DOCUMENT NUMBER: 138:238030  
 TITLE: Preparation of chiral phase-transfer catalysts and their use in diastereoselective preparation of peptides substituted at C $\alpha$  position of N-terminal amino acid residue  
 INVENTOR(S): Maruoka, Keiji  
 PATENT ASSIGNEE(S): Nagase and Co., Ltd., Japan  
 SOURCE: Jpn. Kokai Tokkyo Koho, 18 pp.  
 CODEN: JKXXAF  
 DOCUMENT TYPE: Patent  
 LANGUAGE: Japanese  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 2003081976	A	20030319	JP 2001-301866	20010928
PRIORITY APPLN. INFO.: OTHER SOURCE(S): GI	MARPAT	138:238030	JP 2001-201206	A 20010702



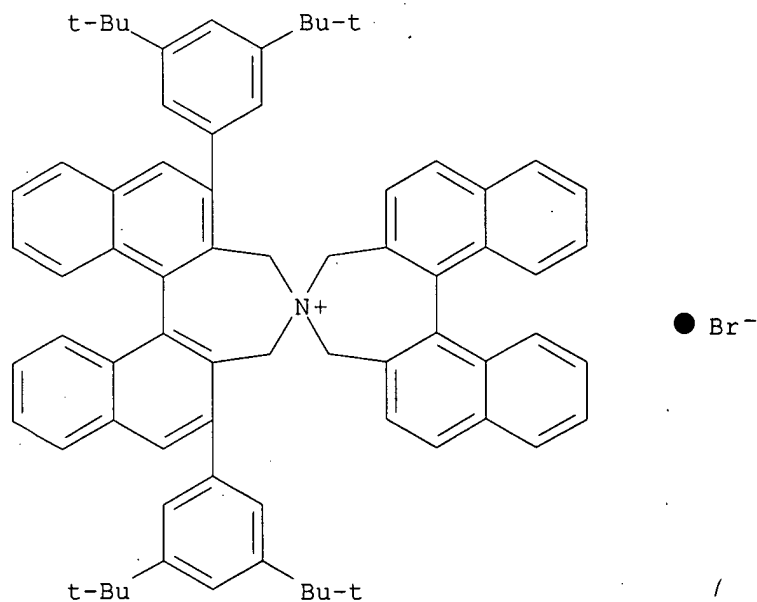
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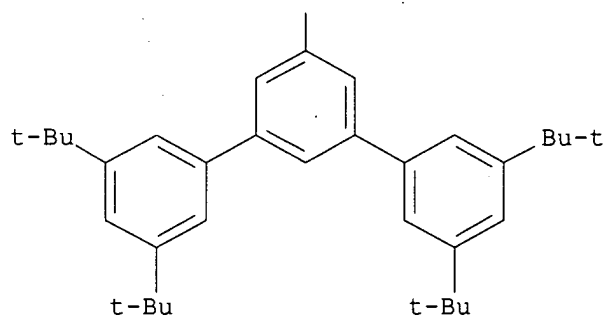
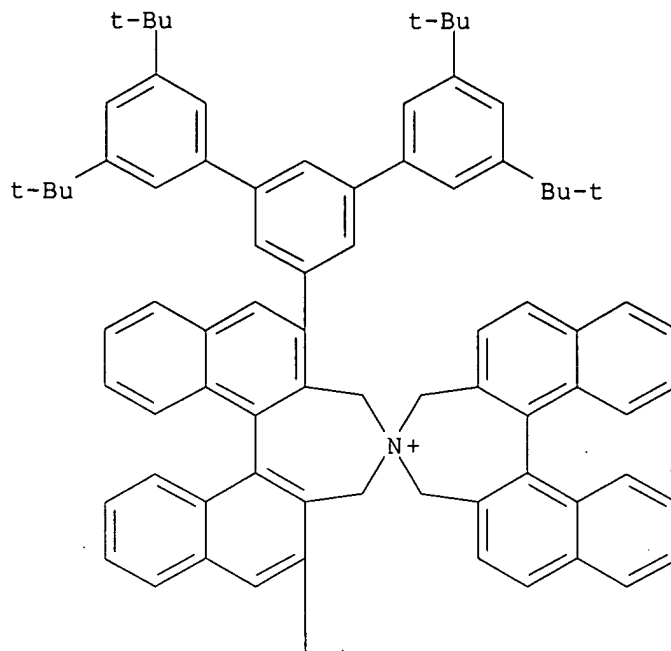
AB N-spiroquaternary ammonium salts I [m, n ≥ 1; when m or n ≥ 2, then Ra, Rb = C1-8 linear or branched alkyl(oxy), C2-8 linear or branched alkenyl, C2-8 alkynyl, halo, (un)substituted aryl; when m = n = 1, then Ra, Rb = (un)substituted aryl; Ar = aryl; X = halo] are prepared R1R2C:NCR3R4COZ [R1, R2 = H, (un)substituted aryl; R1 = R2 ≠ H; R3 = H, C1-6 (branched or cyclic) alkyl(oxy), C2-6 (branched or cyclic) alkenyl, C2-6 (branched or cyclic) alkynyl, (un)substituted (hetero)aryl; Z = α-amino acid or di- or tripeptide (branched or cyclic) C1-6 alkyl ester residue; R4 = C1-10 (branched or cyclic) alkyl, C3-10 (branched or cyclic) (un)substituted aryl, (un)substituted (hetero)aralkyl, etc.], useful as intermediates for antihypertensives, artificial sweeteners, etc., are stereoselectively prepared by treatment of R1R2C:NCHR3COZ (R1-R3, Z = same as above) with R4W (R4 = same as above) in organic solvent-water mixed solvent system in the presence of bases and the chiral N-spiroquaternary ammonium salts as phase-transfer catalysts. Thus, (S)-Ph2C:NCH2CONHCH(CH2Ph)CO2CMe3 was alkylated with EtI in the presence of CsOH and (S,S)-I [Ar = benzene residue, (Ra)n = Ar(Rb)m = 3,5-di(3,5-di-tert-phenyl)] at 0° for 6 h in MePh to give 86% diastereomeric mixture of Ph2C:NCH2CONHCH(CH2Ph)CO2CMe3 with 98% de.

IT 501934-20-9P 501934-21-0P  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
 USES (Uses)  
 (preparation of N-spiroquaternary ammonium salts as chiral phase-transfer catalysts for diastereoselective preparation of modified peptides)

RN 501934-20-9 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(1,1-dimethylethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide (1:1), (11bS,11'bs)-(CA INDEX NAME)

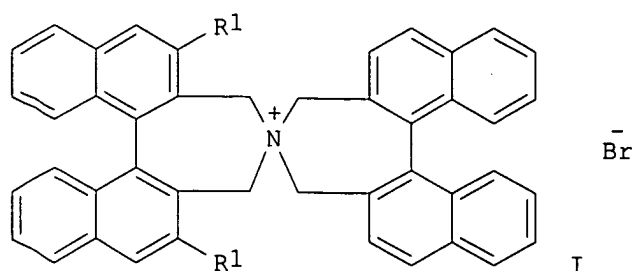


RN 501934-21-0 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[3,3'',5,5''-tetrakis(1,1-dimethylethyl)[1,1':3',1''-terphenyl]-5'-yl]-, bromide (1:1), (11bS,11'bs)- (CA INDEX NAME)



L3 ANSWER 62 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2003:137339 CAPLUS  
 DOCUMENT NUMBER: 139:7158  
 TITLE: Highly stereoselective N-terminal functionalization of  
 small peptides by chiral phase-transfer catalysis  
 AUTHOR(S): Ooi, Takashi; Tayama, Eiji; Maruoka, Keiji  
 CORPORATE SOURCE: Department of Chemistry, Graduate School of Science,  
 Kyoto University, Kyoto, 606-8502, Japan  
 SOURCE: Angewandte Chemie, International Edition (2003),  
 42(5), 579-582  
 CODEN: ACIEF5; ISSN: 1433-7851  
 PUBLISHER: Wiley-VCH Verlag GmbH & Co. KGaA  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 OTHER SOURCE(S): CASREACT 139:7158

GI



AB The optically pure, C2-sym. quaternary ammonium salts I [R1 = 2-naphthalene, 2,3,4-trifluorophenyl, 3,5-di-tert-butylphenyl, 3,5-bis(3,5-di-tert-butylphenyl)phenyl] were prepared and used as the catalysts for asym. phase-transfer catalytic alkylation of peptides. The stereoselective alkylation of dipeptide derivs. Ph2C:NCH2CO-L-AA-Ot-Bu (AA = amino acid), Ph2C:NCH2CO-L(D)-Ala-Ot-Bu and p-ClPhCH:NCH(Me)CO-L-Phe-Ot-Bu was examined and the critical importance of the chiral phase-transfer catalysis in obtaining high stereoselectivity was evaluated.

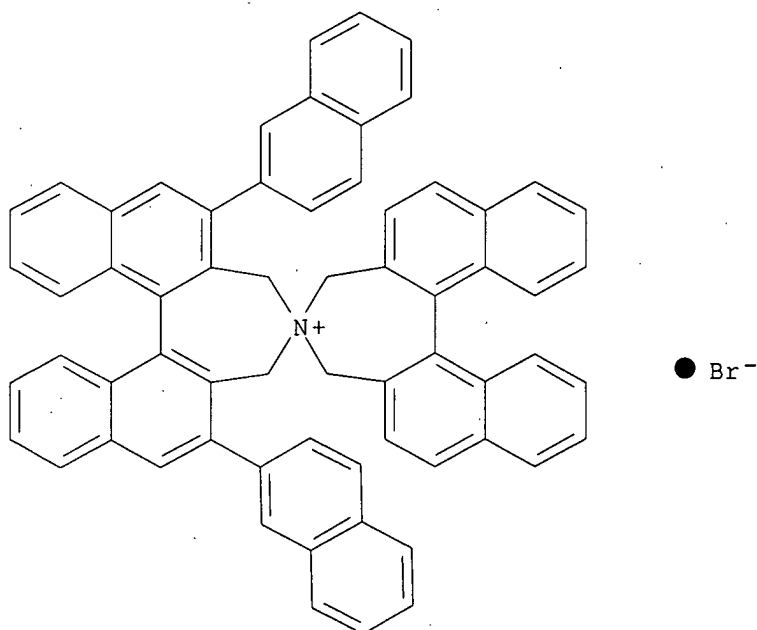
IT 237762-42-4 287384-12-7 466679-91-4  
501934-20-9 501934-21-0 534576-68-6

RL: CAT (Catalyst use); USES (Uses)

(stereoselective alkylation of dipeptide derivs. using chiral quaternary ammonium salts as phase-transfer catalysts)

RN 237762-42-4 CAPLUS

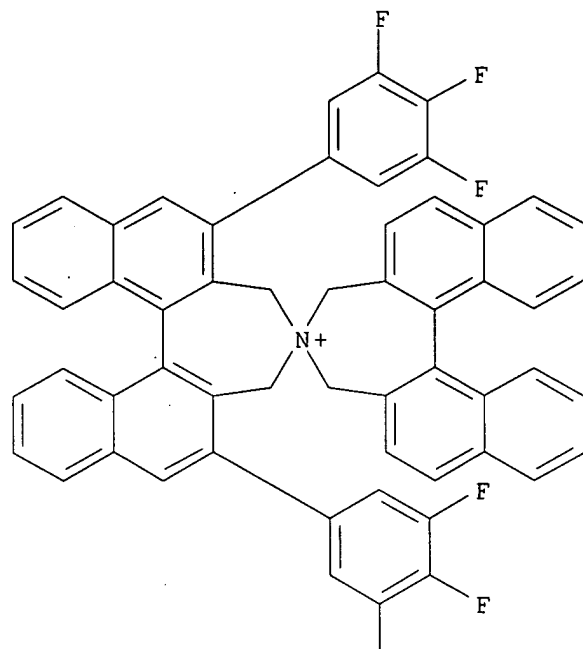
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-di-2-naphthalenyl-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



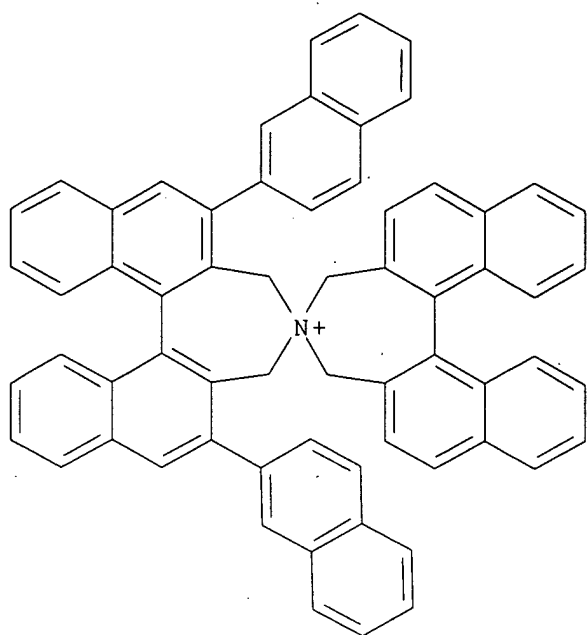
RN 287384-12-7 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)





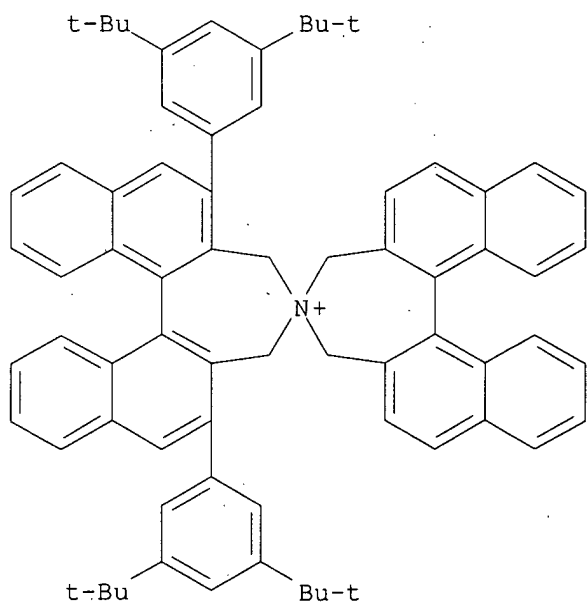
RN 466679-91-4 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
 2,6-di-2-naphthalenyl-, bromide, (11bR,11'bR)- (9CI) (CA INDEX NAME)



● Br<sup>-</sup>

RN 501934-20-9 CAPLUS

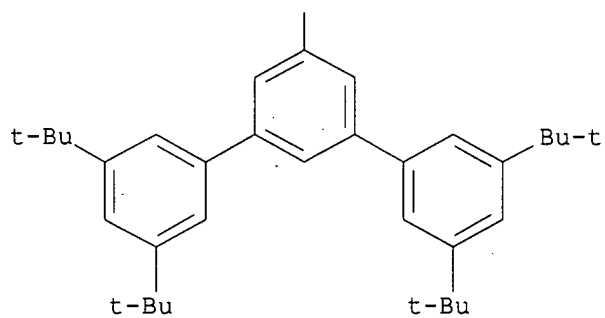
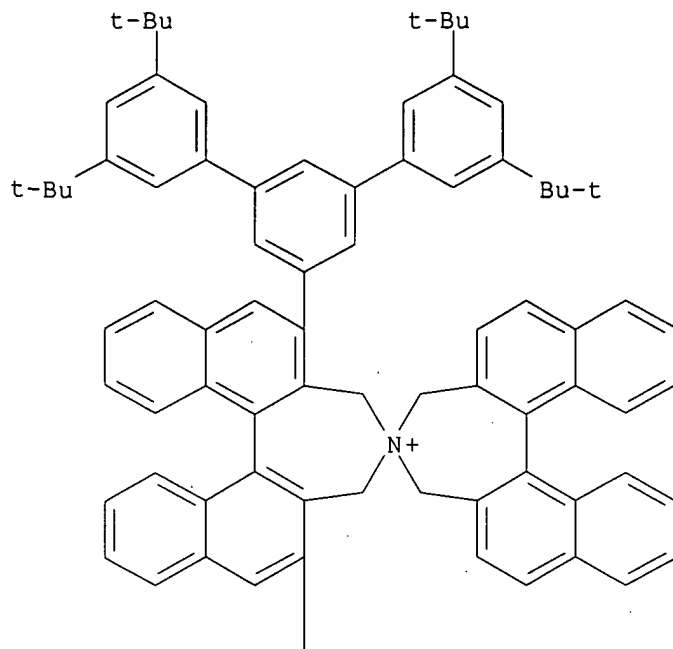
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(1,1-dimethylethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide (1:1), (11bS,11'bs)-(CA INDEX NAME)



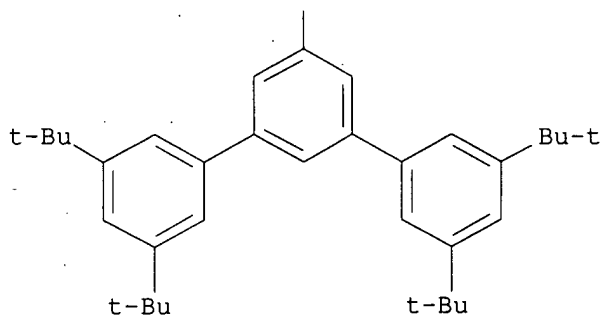
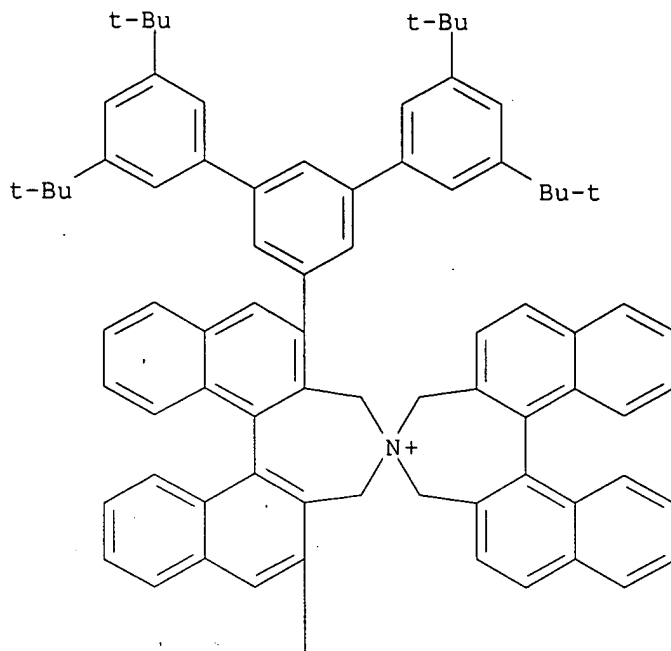
● Br<sup>-</sup>

RN 501934-21-0 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[3,3'',5,5''-tetrakis(1,1-dimethylethyl)[1,1':3',1''-terphenyl]-5'-yl]-, bromide (1:1), (11bS,11'bs)-(CA INDEX NAME)



RN 534576-68-6 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
 2,6-bis[3,3'',5,5''-tetrakis(1,1-dimethylethyl)[1,1':3',1''-terphenyl]-5'-  
 yl]-, bromide, (11bR,11'bR)- (9CI) (CA INDEX NAME)



REFERENCE COUNT: 54 THERE ARE 54 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 63 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2003:77882 CAPLUS

DOCUMENT NUMBER: 138:271233

TITLE: Designer Chiral Quaternary Ammonium Bifluorides as an Efficient Catalyst for Asymmetric Nitroaldol Reaction of Silyl Nitronates with Aromatic Aldehydes

AUTHOR(S): Ooi, Takashi; Doda, Kanae; Maruoka, Keiji

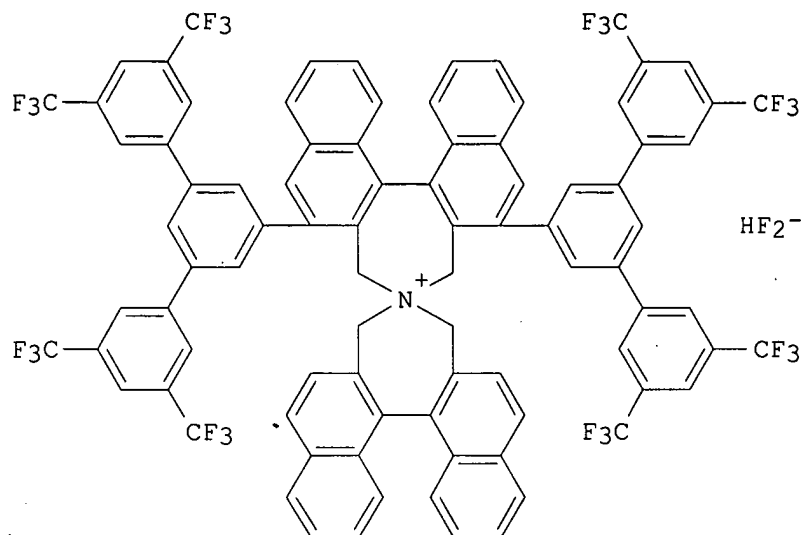
CORPORATE SOURCE: Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto, 606-8502, Japan

SOURCE: Journal of the American Chemical Society (2003), 125(8), 2054-2055

CODEN: JACSAT; ISSN: 0002-7863

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 OTHER SOURCE(S): CASREACT 138:271233  
 GI



I

AB Designer chiral quaternary ammonium bifluoride (S,S)-I was synthesized, and its both catalytic and chiral efficiency were clearly demonstrated by achieving the first catalytic asym. nitroaldol reaction of silyl nitronate with aldehydes. Thus, the reaction of trialkylsilyl nitronates  $R_1CH:N^+(O^-)OSiR_2R_3$  ( $R_1 = Me, Et, PhCH_2OCH_2CH_2$ ;  $R_2 = Me, Et$ ) with aromatic aldehydes  $R_3CHO$  ( $R_3 = Ph, 4-MeC_6H_4, 4-FC_6H_4, 2-naphthyl$ ) in THF in the presence of (S,S)-I proceeded smoothly at  $-78^\circ$ , giving the corresponding nitroaldol adducts  $R_1CHNO_2CH(OH)R_3$  (II) in 70-92% isolated yields. In all the cases, predominant formation of anti-isomers II with high enantioselectivity (up to 97% ee) was observed

IT 503538-63-4P 503538-65-6P

RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)

(asym. synthesis of  $\alpha$ -nitro alcs. via chiral quaternary ammonium bifluoride catalyzed nitroaldol reaction of silyl nitronates with aldehydes)

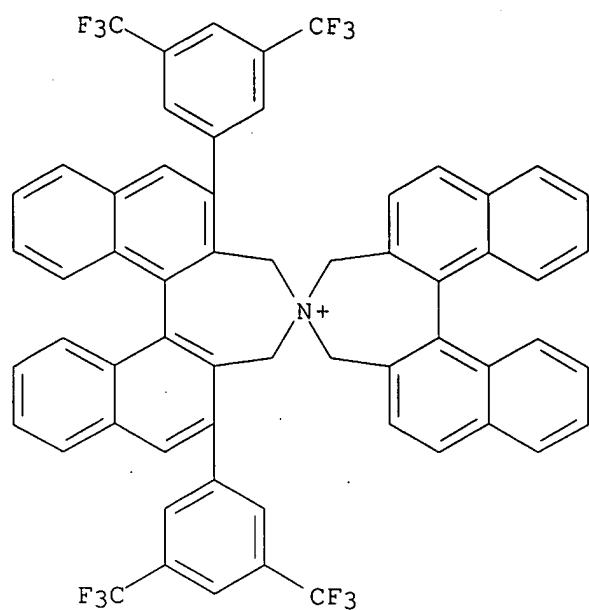
RN 503538-63-4 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, (11bS,11'bs)-, (hydrogen difluoride) (9CI) (CA INDEX NAME)

CM 1

CRN 344550-35-2

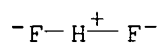
CMF C60 H36 F12 N



CM 2

CRN 18130-74-0

CMF F2 H



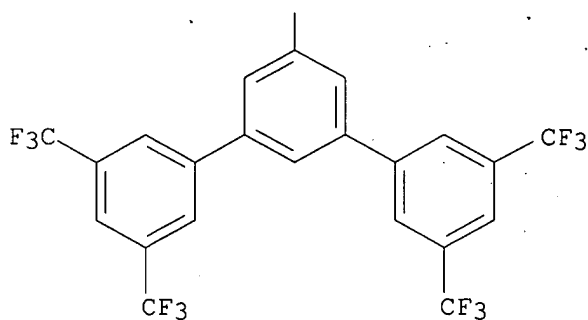
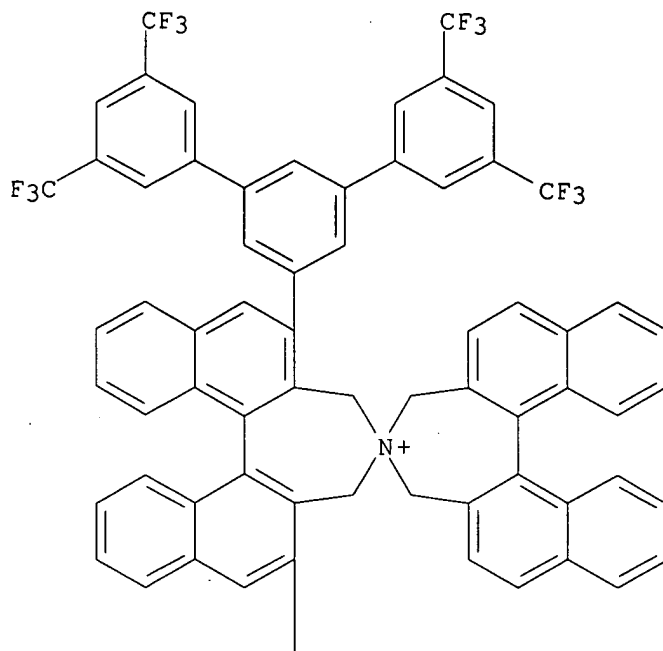
RN 503538-65-6 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[3,3'',5,5''-tetrakis(trifluoromethyl)[1,1':3',1''-terphenyl]-5'-yl]-, (11bS,11'bS)-, (hydrogen difluoride) (9CI) (CA INDEX NAME)

CM 1

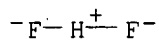
CRN 503538-64-5

CMF C88 H48 F24 N



CM 2

CRN 18130-74-0  
CMF F2 H



IT 438002-03-0 503538-60-1

RL: RCT (Reactant); RACT (Reactant or reagent)

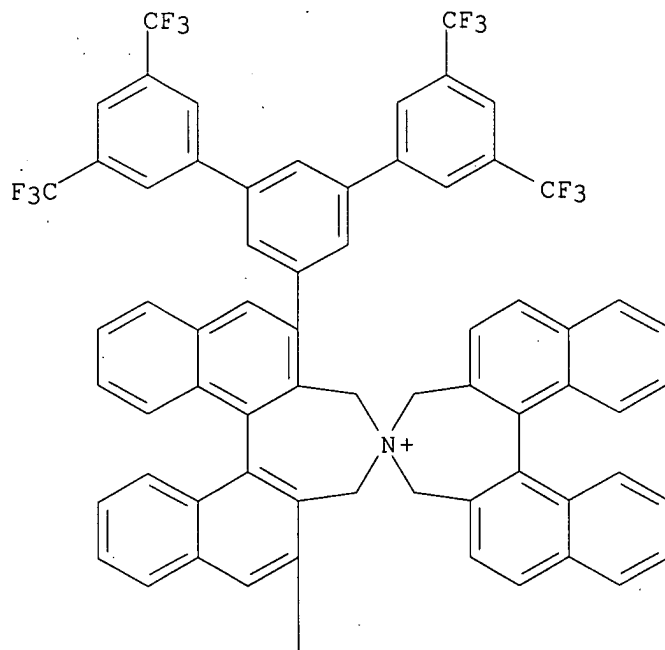
(asym. synthesis of  $\alpha$ -nitro alcs. via chiral quaternary ammonium  
bifluoride catalyzed nitroaldol reaction of silyl nitronates with  
aldehydes)

RN 438002-03-0 CAPLUS

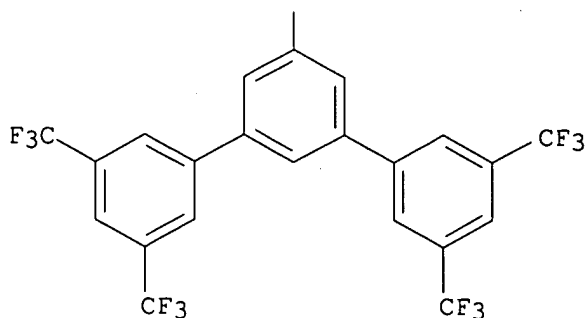
CN 8,8'-Spirobi[8H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-  
bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide (1:1),  
(11bS,11'bS)- (CA INDEX NAME)



PAGE 1-A

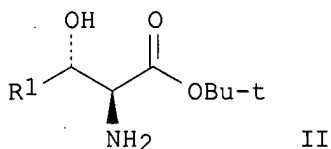
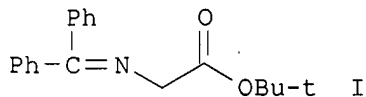






REFERENCE COUNT: 10 THERE ARE 10 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 64 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2002:973631 CAPLUS  
 DOCUMENT NUMBER: 138:338430  
 TITLE: Direct asymmetric aldol reactions of glycine schiff base with aldehydes catalyzed by chiral quaternary ammonium salts  
 AUTHOR(S): Ooi, Takashi; Taniguchi, Mika; Kameda, Minoru; Maruoka, Keiji  
 CORPORATE SOURCE: Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo, Kyoto, 606-8502, Japan  
 SOURCE: Angewandte Chemie, International Edition (2002), 41(23), 4542-4544  
 CODEN: ACIEF5; ISSN: 1433-7851  
 PUBLISHER: Wiley-VCH Verlag GmbH & Co. KGaA  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 OTHER SOURCE(S): CASREACT 138:338430  
 GI



AB A practical and environmentally friendly chemical process for the synthesis of optically active  $\beta$ -hydroxy- $\alpha$ -amino acids, which involves the reaction of glycine Schiff base I with aldehyde acceptors in the presence of catalytic N-spiro chiral quaternary ammonium bromide under mild organic/aqueous biphasic conditions is developed. The cross-aldol products II [R1 = (CH<sub>2</sub>)<sub>2</sub>Ph, (CH<sub>2</sub>)<sub>5</sub>Me, CH<sub>2</sub>Si(i-Pr)<sub>3</sub>, Me, etc] are obtained with excellent stereochem. control.

IT 438002-03-0 503538-60-1 515137-97-0  
 515137-98-1

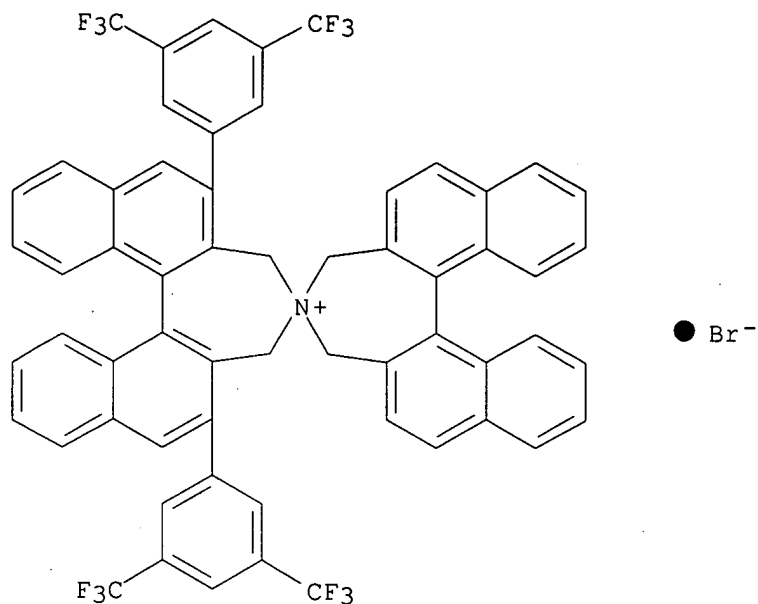
RL: CAT (Catalyst use); USES (Uses)

(asym. synthesis of  $\beta$ -hydroxy amino acids by aldol condensation of glycine schiff base with aldehydes catalyzed by chiral quaternary ammonium salts under phase transfer conditions)

RN 438002-03-0 CAPLUS

CN 8,8'-Spirobi[8H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-

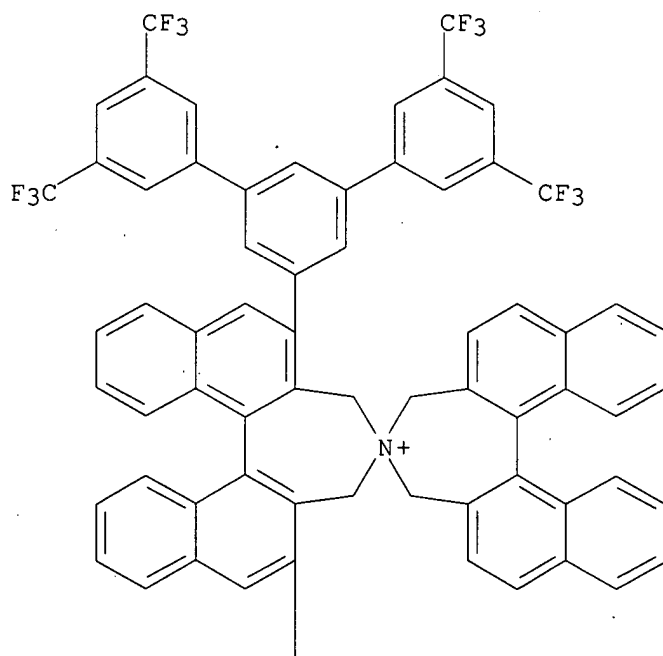
bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide (1:1),  
(11bS,11'bS)- (CA INDEX NAME)

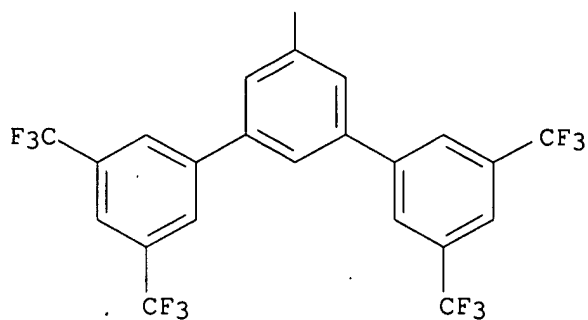


RN 503538-60-1 CAPLUS

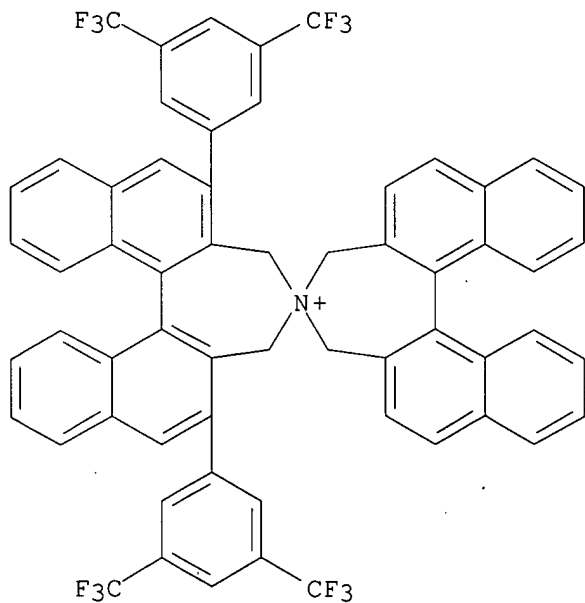
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[3,3'',5,5''-tetrakis(trifluoromethyl)[1,1':3',1''-terphenyl]-5'-yl]-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)

PAGE 1-A

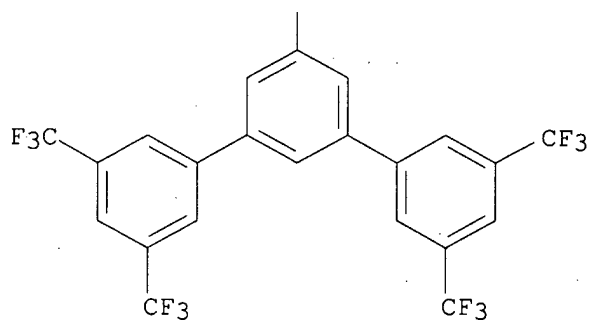
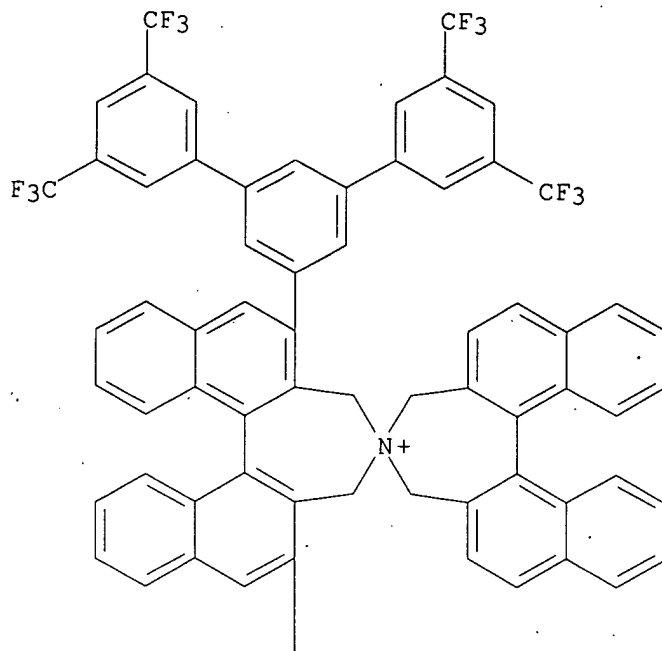




RN 515137-97-0 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide (1:1), (11bR,11'bR)- (CA INDEX NAME)



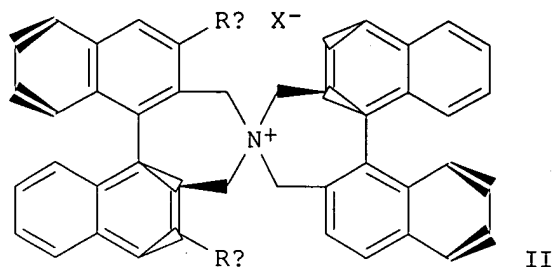
RN 515137-98-1 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[3,3'',5,5''-tetrakis(trifluoromethyl)[1,1':3',1''-terphenyl]-5'-yl]-, bromide, (11bR,11'bR)- (9CI) (CA INDEX NAME)



REFERENCE COUNT: 45 THERE ARE 45 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 65 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2002:686487 CAPLUS  
 DOCUMENT NUMBER: 137:216763  
 TITLE: Preparation of optically active  $\alpha$ -amino ketones  
 INVENTOR(S): Maruoka, Keiji  
 PATENT ASSIGNEE(S): Nippon Soda Co., Ltd., Japan  
 SOURCE: Jpn. Kokai Tokkyo Koho, 7 pp.  
 CODEN: JKXXAF  
 DOCUMENT TYPE: Patent  
 LANGUAGE: Japanese  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 2002255912	A	20020911	JP 2001-50952	20010226
PRIORITY APPLN. INFO.:			JP 2001-50952	20010226
OTHER SOURCE(S):	MARPAT 137:216763			
GI				



AB Optically active  $R_1COCHR_2NH_2$  [I;  $R_1, R_2 = H, \text{ alkyl, (un)substituted aryl, (un)substituted heteroaryl, (un)substituted aralkyl}$ ] are prepared by treatment of  $R_1C(:NOR_3)CH_2R_2$  ( $R_1, R_2 = \text{same as I; } R_3 = \text{leaving group}$ ) with bases in the presence of optically active phase-transfer catalysts and lower alcs. and treatment with acids. Anti-deoxybenzoin oxime was treated with KOH in MeOH-PhMe in the presence of p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl and phase-transfer catalyst II ( $R_a = \beta\text{-naphthyl}$ ) at 0° for 4 h and treated with HCl at 0° for 2 h to give 53% optically active I ( $R_1 = R_2 = Ph$ ) with 30% ee.

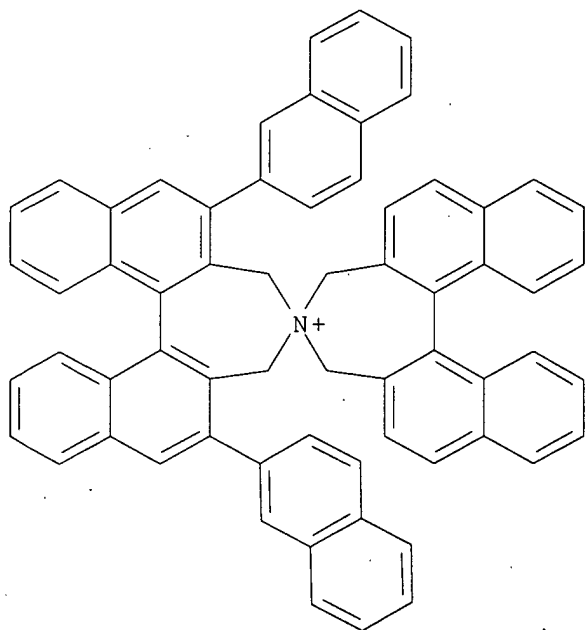
IT 344550-37-4

RL: CAT (Catalyst use); USES (Uses)

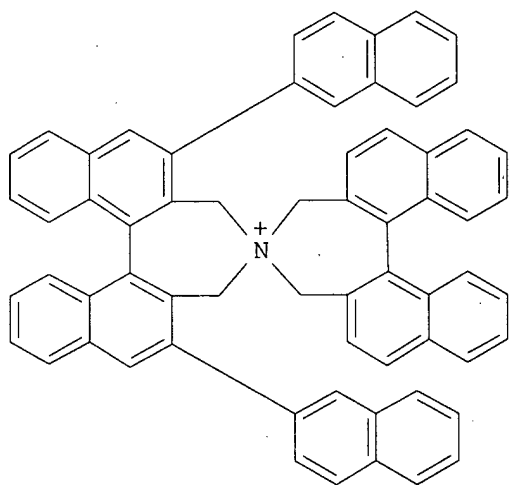
(catalyst; preparation of optically active  $\alpha$ -amino ketones from oximes)

RN 344550-37-4 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-di-2-naphthalenyl-, (11bS,11'bS)- (9CI) (CA INDEX NAME)



L3 ANSWER 66 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2002:519351 CAPLUS  
 DOCUMENT NUMBER: 137:279434  
 TITLE: Evaluation of the efficiency of the chiral quaternary ammonium salt  $\beta$ -Np-NAS-Br in the organic-aqueous phase-transfer alkylation of a protected glycine derivative  
 AUTHOR(S): Ooi, Takashi; Uematsu, Yukitaka; Maruoka, Keiji  
 CORPORATE SOURCE: Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto, 606-8502, Japan  
 SOURCE: Advanced Synthesis & Catalysis (2002), 344(3+4), 288-291  
 CODEN: ASCAF7; ISSN: 1615-4150  
 PUBLISHER: Wiley-VCH Verlag GmbH  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 OTHER SOURCE(S): CASREACT 137:279434  
 GI



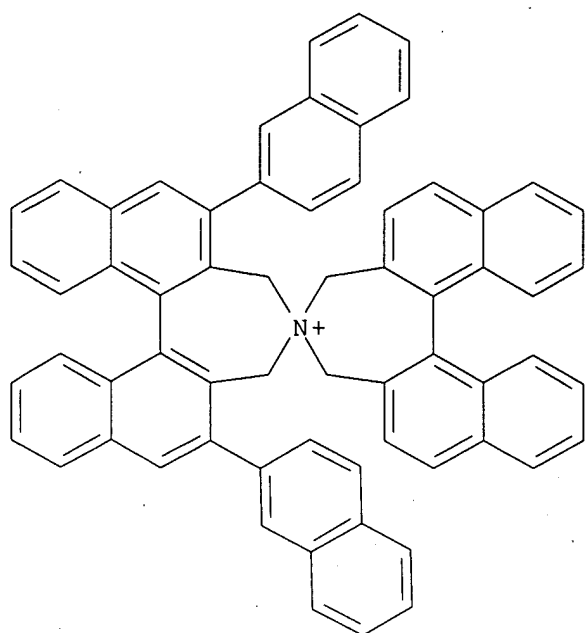
I

AB The inherent efficiency of the N-spiro C2-sym. chiral quaternary ammonium salt (S,S)-I-Br [(S,S)- $\beta$ -Np-NAS-Br] has been evaluated in the representative organic-aqueous liquid-liquid phase-transfer benzylation and allylation of glycine tert-Bu ester benzophenone Schiff base Ph2C:NCH2COOCHMe3. This revealed the practical conditions for the asym. synthesis of both natural and unnatural  $\alpha$ -amino acids, whose usefulness was demonstrated by the formal enantioselective synthesis of antibiotic L-azatyrosine.

IT 237762-42-4 466679-91-4 466679-93-6  
 RL: CAT (Catalyst use); USES (Uses)  
 (phase-transfer alkylation of protected glycine derivative using chiral quaternary ammonium salt as catalyst in organic-aqueous)

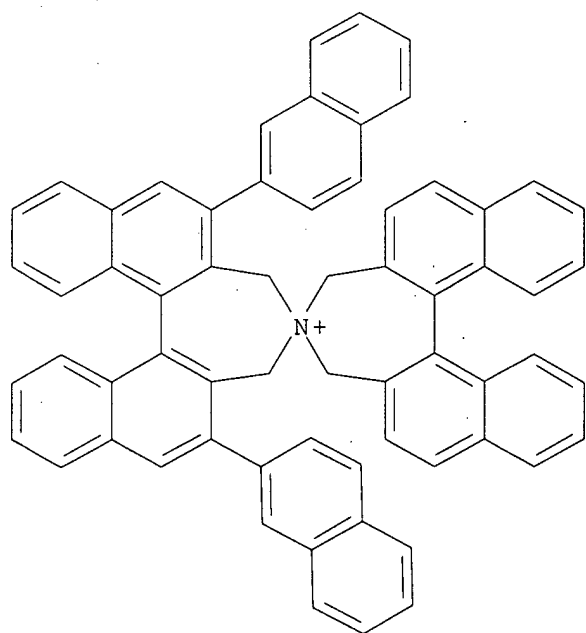
RN 237762-42-4 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-di-2-naphthalenyl-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



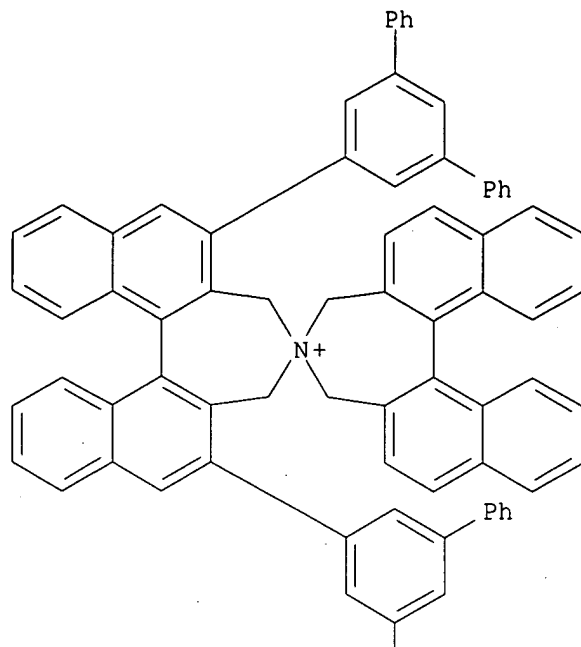
● Br<sup>-</sup>

RN 466679-91-4 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-di-2-naphthalenyl-, bromide, (11bR,11'bR)- (9CI) (CA INDEX NAME)



● Br<sup>-</sup>

RN 466679-93-6 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis([1,1':3',1''-terphenyl]-5'-yl)-3,3',5,5'-tetrahydro-, bromide (1:1), (11bR,11'bR)- (CA INDEX NAME)

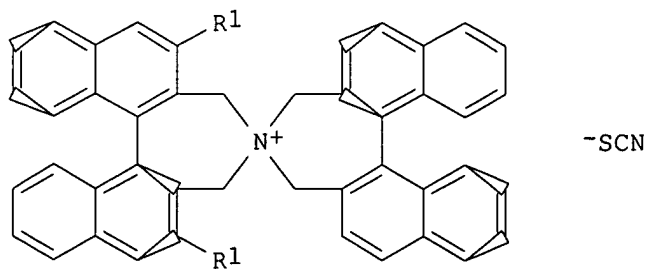


REFERENCE COUNT: 27 THERE ARE 27 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 67 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2002:464180 CAPLUS  
 DOCUMENT NUMBER: 137:47130  
 TITLE: Preparation of optically active azoniaspirotridecane salts and preparation of  $\beta$ -hydroxyketones by using them  
 INVENTOR(S): Maruoka, Keiji  
 PATENT ASSIGNEE(S): Nagase and Co., Ltd., Japan  
 SOURCE: Jpn. Kokai Tokkyo Koho, 32 pp.  
 CODEN: JKXXAF  
 DOCUMENT TYPE: Patent  
 LANGUAGE: Japanese  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 2002173492	A	20020621	JP 2000-372291	20001207
PRIORITY APPLN. INFO.:			JP 2000-372291	20001207
OTHER SOURCE(S):		CASREACT 137:47130; MARPAT 137:47130		
GI				





AB The compds. I (R1, R2 = H, C1-6 alkyl, C2-6 alkenyl, C2-6 alkynyl, aralkyl, etc.) are prepared  $\beta$ -Hydroxyketones are prepared by stereoselective reaction of silyl enol ethers with carbonyl compds. in the presence of reaction products prepared by ion-exchanging I (R1, R2 = same as above) with H2SO4 and treated with alkali metal fluorides. I [R1 = R2 = 3,5-bis(trifluoromethyl)phenyl] was treated with H2SO4 in H2O at 75° for 1 h to give [(S)-3,3'-bis[di(3,5-trifluoromethyl)phenyl]-1,1'-binaphthyl-2,2'-dimethylammonium]spiro[(S)-1,1'-binaphthyl-2,2'-dimethylamine] bisulfate, which was treated with KF in THF at room temperature for 1 h and mixed with benzaldehyde, 4-trimethylsilyloxy-1,2-dihydronaphthalene, and PhMe -78° to -40° for 1 h to give 90% (2R,1'R)-2-(1'-hydroxy-1'-phenylmethyl)-1-tetralone.

IT 237762-42-4 287384-12-7

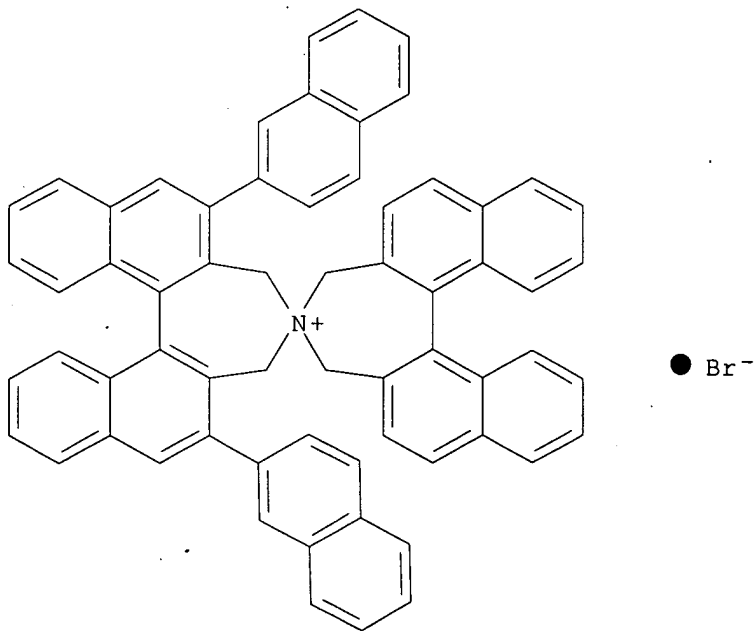
RL: RCT (Reactant); RACT (Reactant or reagent)

(preparation of catalyst; preparation of optically active azoniaspirotridecane

salts and preparation of  $\beta$ -hydroxyketones by using them)

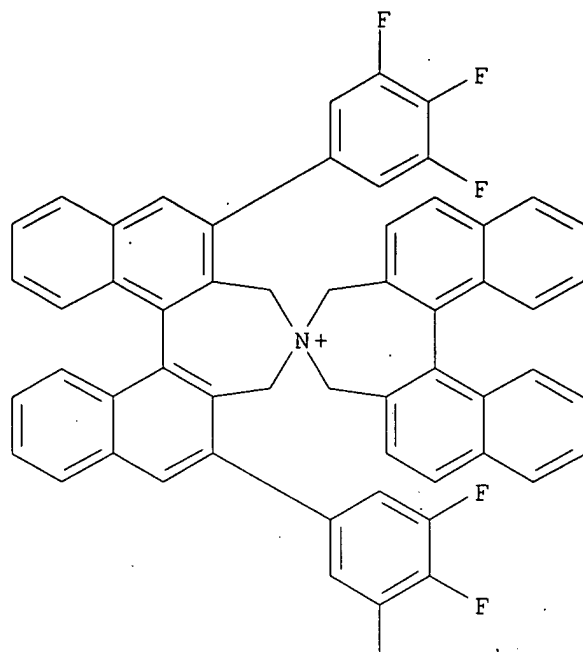
RN 237762-42-4 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-di-2-naphthalenyl-, bromide (1:1), (11bS,11'BS)- (CA INDEX NAME)



RN 287384-12-7 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'BS)- (CA INDEX NAME)



IT 344550-36-3P 344550-38-5P 438001-94-6P  
438001-95-7P 438001-96-8P 438002-03-0P  
438002-04-1P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT  
(Reactant or reagent)

(preparation of catalyst; preparation of optically active  
azoniaspirotridecane  
salts and preparation of  $\beta$ -hydroxyketones by using them)

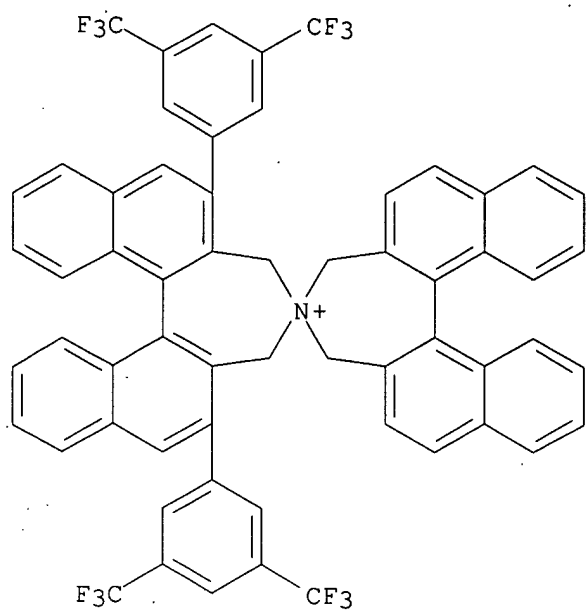
RN 344550-36-3 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-  
bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, (11bS,11'BS)-, sulfate  
(1:1) (9CI) (CA INDEX NAME)

CM 1

CRN 344550-35-2

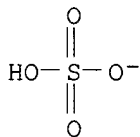
CMF C60 H36 F12 N



CM 2

CRN 14996-02-2

CMF H O4 S



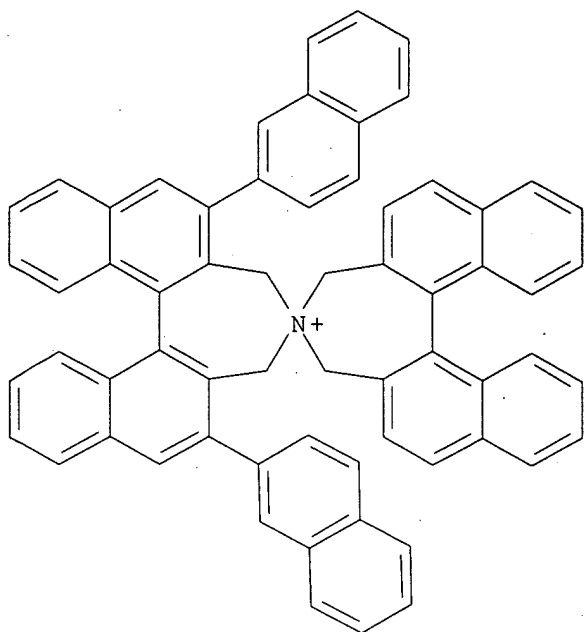
RN 344550-38-5 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-di-2-naphthalenyl-, (11bS,11'bS)-, sulfate (1:1) (9CI) (CA INDEX NAME)

CM 1

CRN 344550-37-4

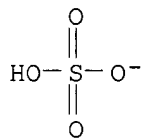
CMF C64 H44 N



CM 2

CRN 14996-02-2

CMF H O4 S



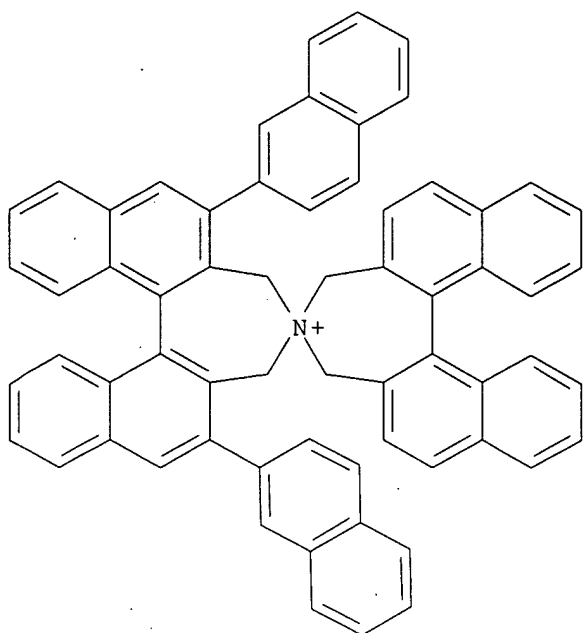
RN 438001-94-6 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-di-2-naphthalenyl-, (11bS,11'bS)-, thiocyanate (9CI) (CA INDEX NAME)

CM 1

CRN 344550-37-4

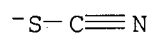
CMF C64 H44 N



CM 2

CRN 302-04-5

CMF C N S



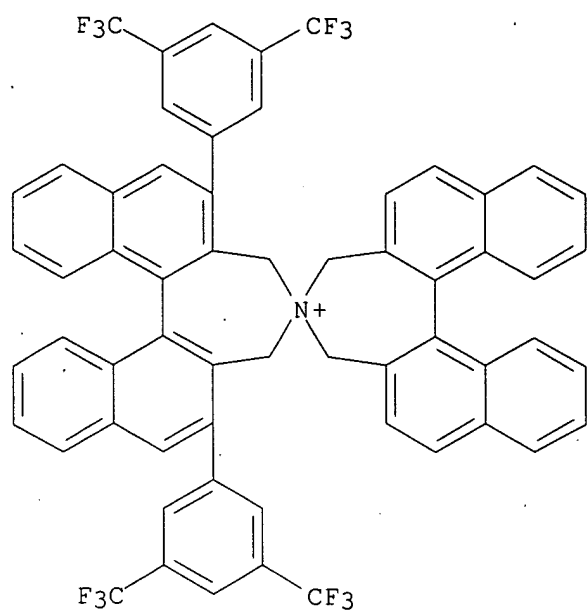
RN 438001-95-7 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, (11bS,11'bS)-, thiocyanate (9CI) (CA INDEX NAME)

CM 1

CRN 344550-35-2

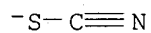
CMF C60 H36 F12 N



CM 2

CRN 302-04-5

CMF C N S



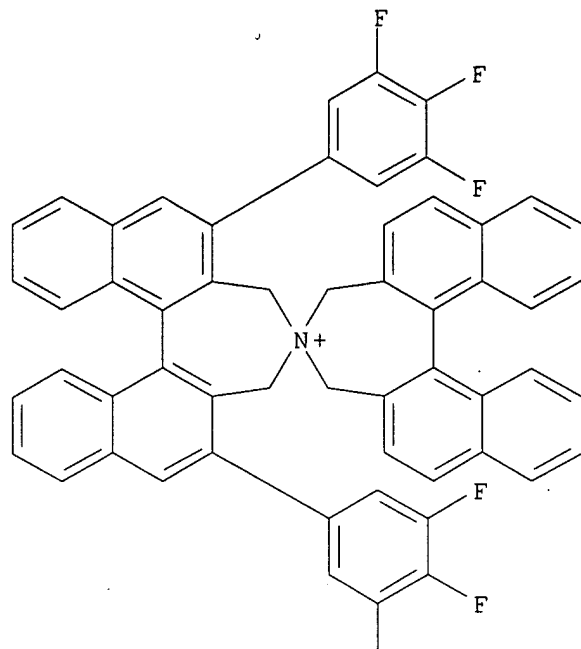
RN 438001-96-8 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, (11bS,11'bS)-, thiocyanate (9CI) (CA INDEX NAME)

CM 1

CRN 401846-45-5

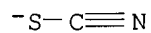
CMF C56 H34 F6 N



CM 2

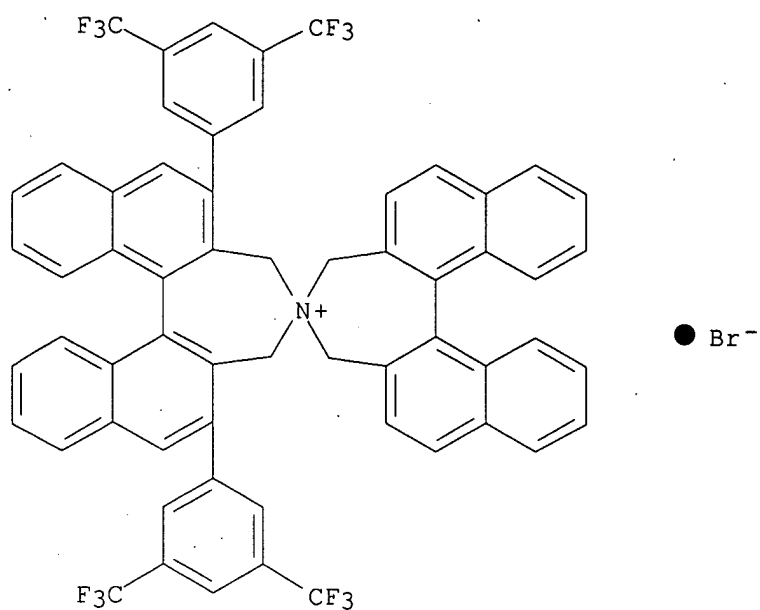
CRN 302-04-5

CMF C N S



RN 438002-03-0 CAPLUS

CN 8,8'-Spirobi[8H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)

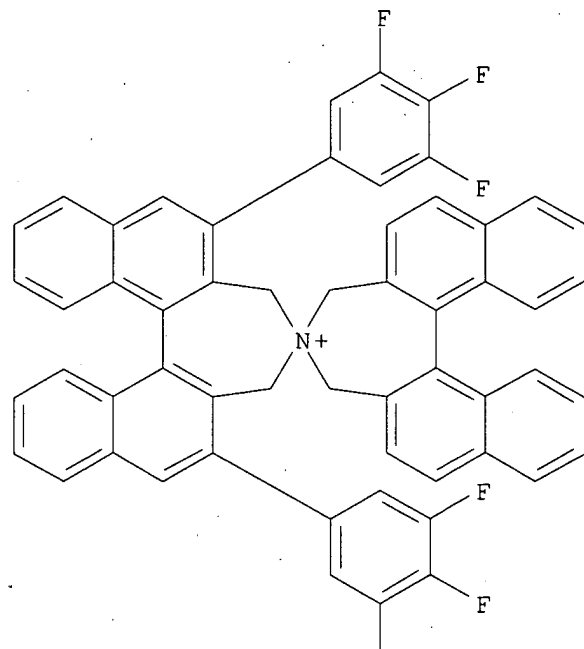


RN 438002-04-1 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
 2,6-bis(3,4,5-trifluorophenyl)-, (11bS,11'bs)-, sulfite (1:1) (9CI) (CA  
 INDEX NAME)

CM 1

CRN 401846-45-5  
 CMF C56 H34 F6 N

PAGE 1-A



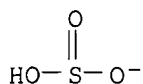


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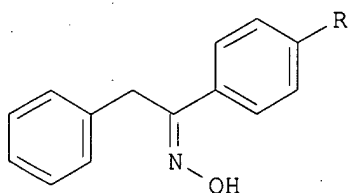
CM 2

CRN 15181-46-1

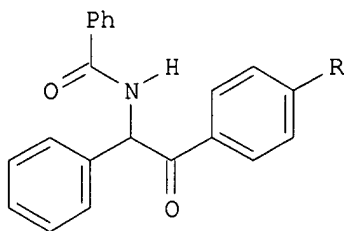
CMF H O3 S



L3 ANSWER 68 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2002:422156 CAPLUS  
 DOCUMENT NUMBER: 137:154682  
 TITLE: Asymmetric Induction in the Neber Rearrangement of Simple Ketoxime Sulfonates under Phase-Transfer Conditions: Experimental Evidence for the Participation of an Anionic Pathway  
 AUTHOR(S): Ooi, Takashi; Takahashi, Makoto; Doda, Kanae; Maruoka, Keiji  
 CORPORATE SOURCE: Department of Chemistry Graduate School of Science, Kyoto University, Sakyo Kyoto, 606-8502, Japan  
 SOURCE: Journal of the American Chemical Society (2002), 124(26), 7640-7641  
 CODEN: JACSAT; ISSN: 0002-7863  
 PUBLISHER: American Chemical Society  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 OTHER SOURCE(S): CASREACT 137:154682  
 GI



I



II

AB Phase-transfer catalysis has been successfully utilized for the Neber rearrangement of simple ketoxime sulfonates. Thus, treatment of (Z)-oxime I (R = H) with 4-MeC6H4SO2Cl (1.2 equiv) in the presence of Bu4NBr (5 mol %) and MeOH (10 equiv) in toluene-50% KOH aqueous solution (volume ratio = 3:1) at 0° for 2 h. followed by benzoylation and acidic hydrolysis afforded the protected  $\alpha$ -amino ketone II in 80% isolated yield. Similar rearrangement under phase-transfer conditions, using a structurally rigid, C2-sym. chiral quaternary ammonium bromide as a catalyst, gave (S)-II (R = H) in 80% yield and with 51% ee. Enhanced enantioselectivity (63% ee) was observed in the rearrangement of the oxime sulfonate derived from (Z)-oxime I (R = F), and notably, use of mesitylene in place of toluene further increased the enantioselectivity to 70% ee. The reaction with (E)-isomer of I (R = H) afforded racemic II in 61% yield.

IT 446017-35-2 446017-36-3

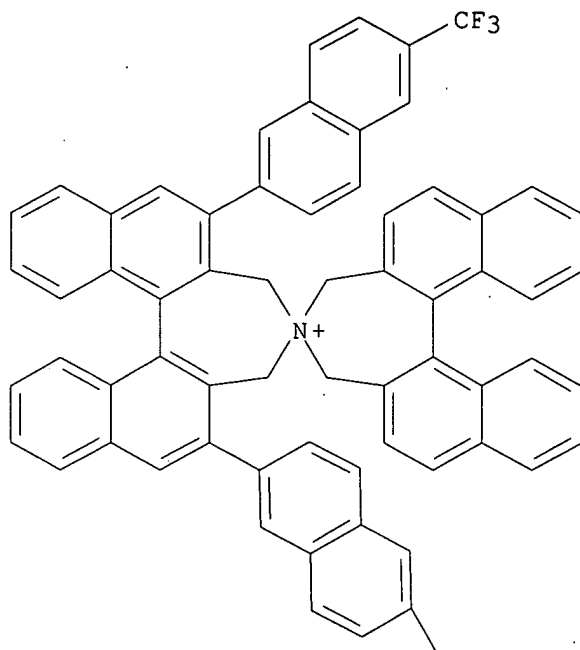
RL: CAT (Catalyst use); USES (Uses)

(asym. synthesis of (amino)diaryl ketones via ketone oximation and quaternary ammonium bromide catalyzed Neber rearrangement of ketoxime sulfonates under phase-transfer conditions)

RN 446017-35-2 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[6-(trifluoromethyl)-2-naphthalenyl]-, bromide, (11bS,11'bS)- (9CI) (CA INDEX NAME)

PAGE 1-A

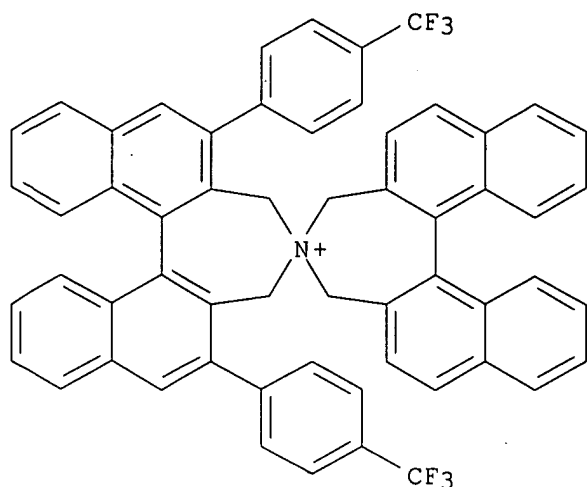


PAGE 2-A



RN 446017-36-3 CAPLUS

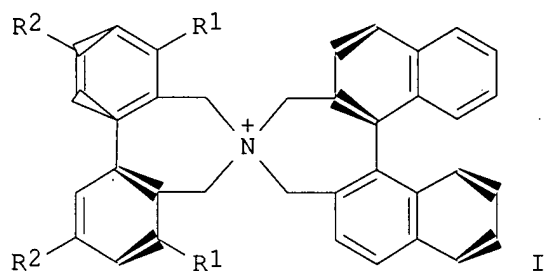
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis[4-(trifluoromethyl)phenyl]-, bromide, (11bS,11'bS)- (9CI) (CA INDEX NAME)



● Br<sup>-</sup>

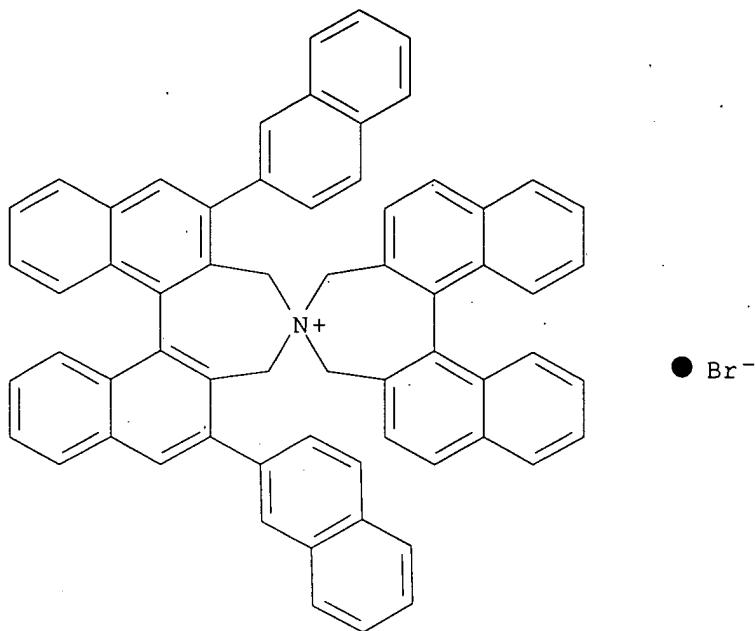
REFERENCE COUNT: 26 THERE ARE 26 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 69 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2002:385687 CAPLUS  
 DOCUMENT NUMBER: 137:185143  
 TITLE: Conformationally flexible, chiral quaternary ammonium bromides for asymmetric phase-transfer catalysis  
 AUTHOR(S): Ooi, Takashi; Uematsu, Yukitaka; Kameda, Minoru; Maruoka, Keiji  
 CORPORATE SOURCE: Department of Chemistry Graduate School of Science, Kyoto University, Kyoto, 606-8502, Japan  
 SOURCE: Angewandte Chemie, International Edition (2002), 41(9), 1551-1554  
 CODEN: ACIEF5; ISSN: 1433-7851  
 PUBLISHER: Wiley-VCH Verlag GmbH  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 OTHER SOURCE(S): CASREACT 137:185143  
 GI

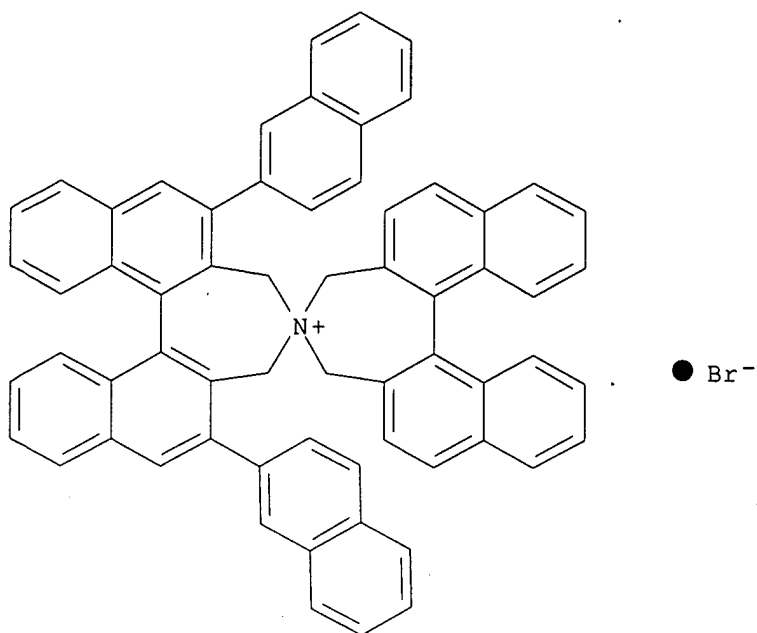


AB A simple yet powerful strategy for the mol. design of chiral phase-transfer catalysts: conformationally flexible, N-spiro chiral quaternary ammonium bromides (I.Br<sup>-</sup>) have been newly designed and are found to exert high chiral efficiency by taking advantage of the considerable difference of activity between the diastereomeric homo- and

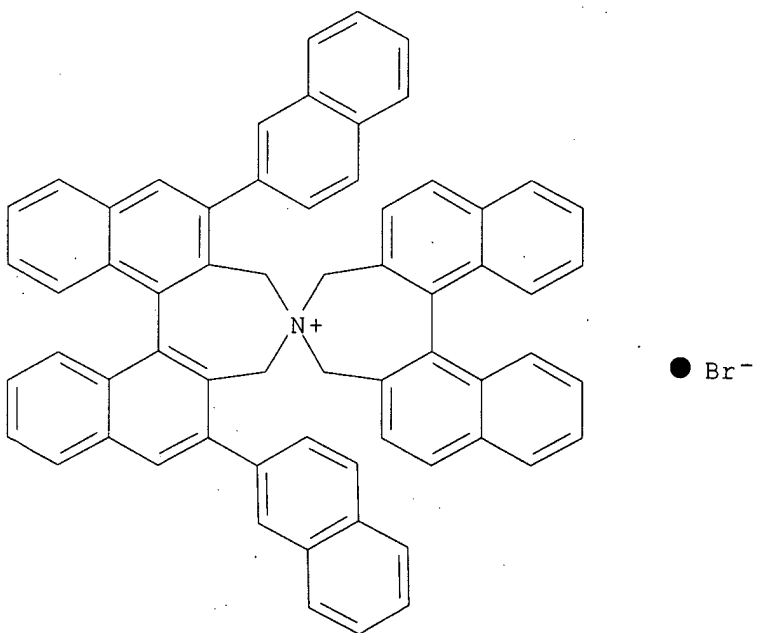
heterochiral isomers through rapid conformational interconversion.  
 IT 237762-42-4  
 RL: CAT (Catalyst use); USES (Uses)  
 (conformationally flexible N-spiro chiral binaphthyl/biphenyl  
 quaternary ammonium bromides for asym. phase-transfer catalysis)  
 RN 237762-42-4 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
 2,6-di-2-naphthalenyl-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



IT 452067-26-4 452067-27-5  
 RL: CAT (Catalyst use); USES (Uses)  
 (heterochiral catalyst, low ee; conformationally flexible N-spiro  
 chiral binaphthyl/biphenyl quaternary ammonium bromides for asym.  
 phase-transfer catalysis)  
 RN 452067-26-4 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
 2,6-di-2-naphthalenyl-, bromide, (11bR,11'bS)- (CA INDEX NAME)



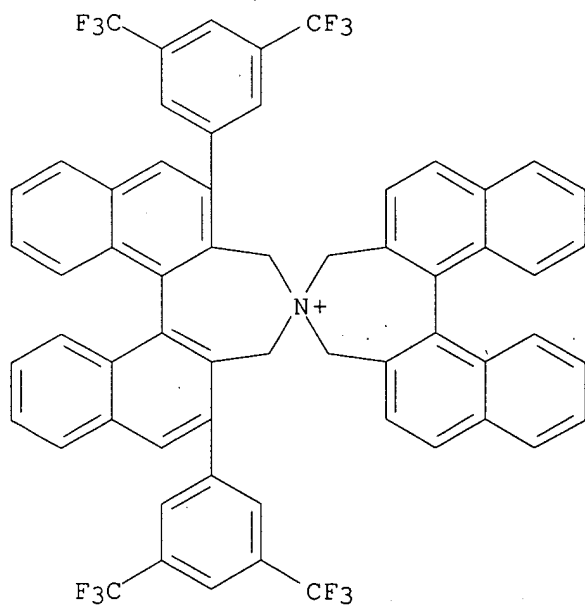
RN 452067-27-5 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-di-2-naphthalenyl-, bromide, (11bS,11'bR)- (9CI) (CA INDEX NAME)



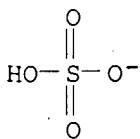
REFERENCE COUNT: 32 THERE ARE 32 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 70 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2001:905551 CAPLUS  
 DOCUMENT NUMBER: 136:294340  
 TITLE: Esterification of carboxylic acids catalyzed by in situ generated tetraalkylammonium fluorides  
 AUTHOR(S): Ooi, Takashi; Sugimoto, Hayato; Doda, Kanae; Maruoka, Keiji  
 CORPORATE SOURCE: Department of Chemistry, Graduate School of Science,

SOURCE: Kyoto University, Sakyo, Kyoto, 606-8502, Japan  
 Tetrahedron Letters (2001), 42(52), 9245-9248  
 CODEN: TELEAY; ISSN: 0040-4039  
 PUBLISHER: Elsevier Science Ltd.  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 OTHER SOURCE(S): CASREACT 136:294340  
 AB Esterification of carboxylic acids with alkyl halides can be efficiently catalyzed by Bu<sub>4</sub>NF (TBAF) generated in situ from Bu<sub>4</sub>N hydrogen sulfate (TBAHSO<sub>4</sub>) and KF·2H<sub>2</sub>O in THF. The general applicability and the characteristic feature of this approach was amply demonstrated.  
 IT 344550-36-3  
 RL: CAT (Catalyst use); USES (Uses)  
 (esterification of carboxylic acids catalyzed by in situ generated tetraalkylammonium fluorides)  
 RN 344550-36-3 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, (11bS,11'bS)-, sulfate (1:1) (9CI) (CA INDEX NAME)  
 CM 1  
 CRN 344550-35-2  
 CMF C60 H36 F12 N

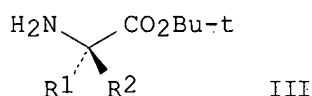
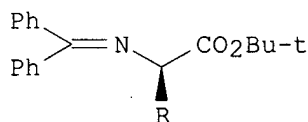
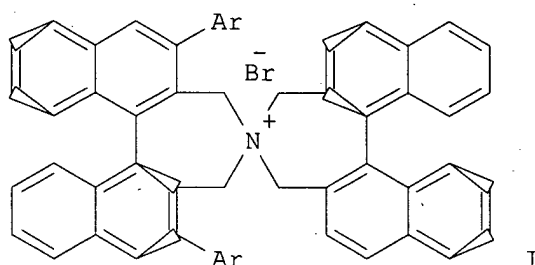


CM 2  
 CRN 14996-02-2  
 CMF H O4 S



REFERENCE COUNT: 15 THERE ARE 15 CITED REFERENCES AVAILABLE FOR THIS

L3 ANSWER 71 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2001:872313 CAPLUS  
 DOCUMENT NUMBER: 136:200448  
 TITLE: Design of new, chiral phase-transfer catalysts for practical, catalytic asymmetric synthesis  
 AUTHOR(S): Maruoka, Keiji  
 CORPORATE SOURCE: Graduate School of Science, Department of Chemistry, Kyoto University, Kyoto, 606-8502, Japan  
 SOURCE: Journal of Fluorine Chemistry (2001), 112(1), 95-99  
 CODEN: JFLCAR; ISSN: 0022-1139  
 PUBLISHER: Elsevier Science S.A.  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 OTHER SOURCE(S): CASREACT 136:200448  
 GI



AB Structurally rigid, chiral spiro ammonium salts I [Ar = H, Ph,  $\beta$ -naphthyl, 3,4,5-trifluorophenyl; derived from com. available (S)-binaphthol] have been designed as new C2-sym. chiral phase-transfer catalysts. I was successfully applied to the highly efficient, catalytic enantioselective alkylation of tert-Bu glycinate Schiff base under mild phase-transfer conditions to furnish  $\alpha$ -alkyl- $\alpha$ -amino acids II (R = CH<sub>2</sub>Ph, Me, Et, CH<sub>2</sub>CH:CH<sub>2</sub>, CH<sub>2</sub>C.tplbond.CH, CH<sub>2</sub>C6H<sub>4</sub>Me-4, CH<sub>2</sub>C6H<sub>4</sub>F-4, 1-naphthylmethyl) and  $\alpha,\alpha$ -dialkyl- $\alpha$ -amino acids III [R<sub>1</sub> = CH<sub>2</sub>CH:CH<sub>2</sub>, CH<sub>2</sub>Ph; R<sub>2</sub> = CH<sub>2</sub>Ph, CH<sub>2</sub>C(Me):CH<sub>2</sub>, CH<sub>2</sub>C.tplbond.CH, CH<sub>2</sub>CH:CH<sub>2</sub>] with excellent enantioselectivity. In addition, quaternary ammonium salts Bu<sub>4</sub>N<sup>+</sup>X<sup>-</sup> (X = I, Br, OTf, etc.) have been utilized for the in situ generation of chiral quaternary ammonium fluorides Bu<sub>4</sub>N<sup>+</sup>F<sup>-</sup>.

IT 344550-36-3 344550-38-5 401846-46-6  
 RL: CAT (Catalyst use); RCT (Reactant); RACT (Reactant or reagent); USES (Uses)  
 (anion exchange-mediated preparation of quaternary ammonium fluoride salts as phase transfer catalysts for asym. aldol condensation reactions)

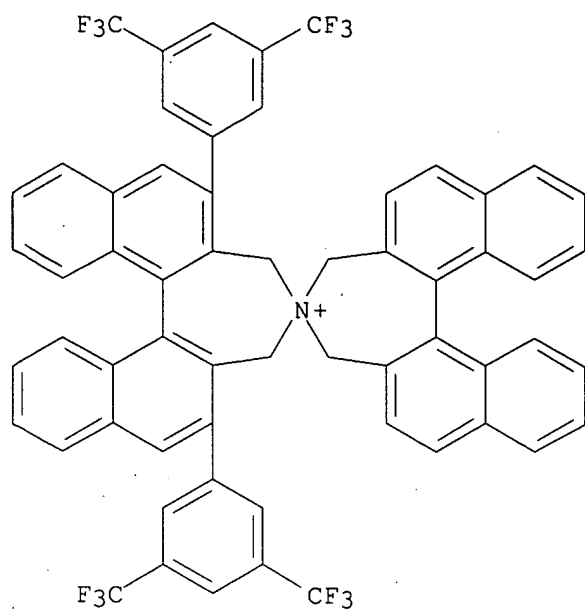
RN 344550-36-3 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, (11bS,11'bS)-, sulfate (1:1) (9CI) (CA INDEX NAME)

CM 1

CRN 344550-35-2

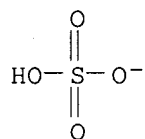
CMF C60 H36 F12 N



CM 2

CRN 14996-02-2

CMF H O4 S



RN 344550-38-5 CAPLUS

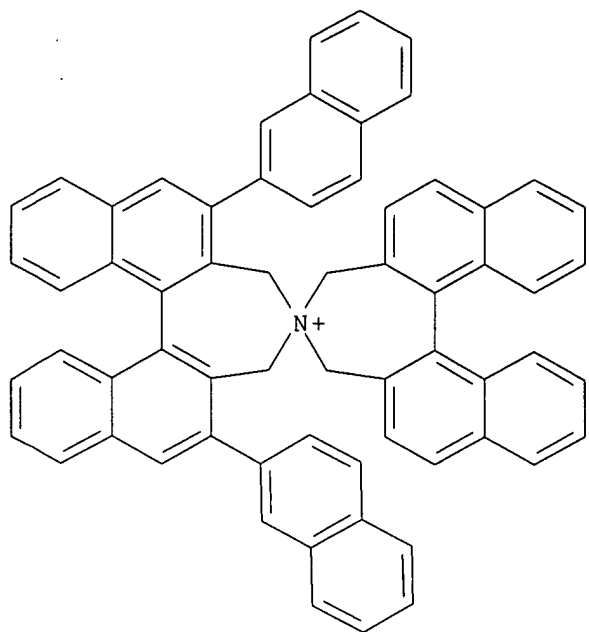
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-di-2-naphthalenyl-, (11bS,11'bS)-, sulfate (1:1) (9CI) (CA INDEX NAME)

CM 1

CRN 344550-37-4

CMF C64 H44 N

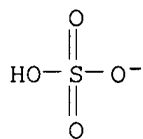




CM 2

CRN 14996-02-2

CMF H O4 S



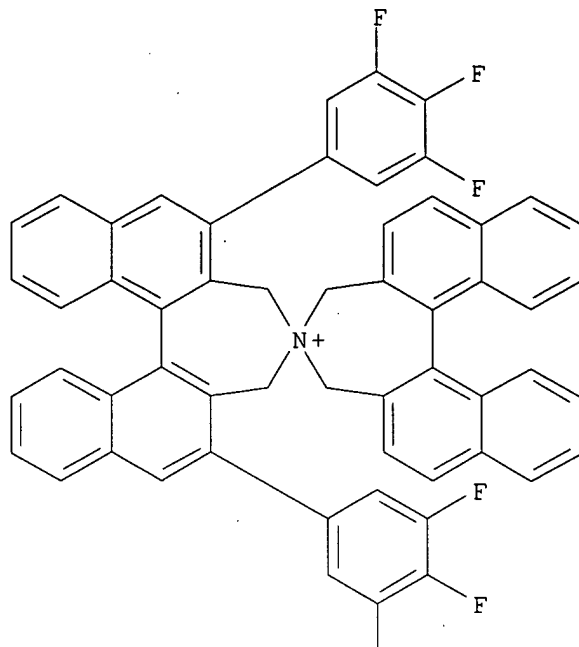
RN 401846-46-6 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, stereoisomer, sulfate (1:1) (9CI) (CA INDEX NAME)

CM 1

CRN 401846-45-5

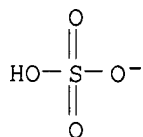
CMF C56 H34 F6 N



CM 2

CRN 14996-02-2

CMF H O4 S



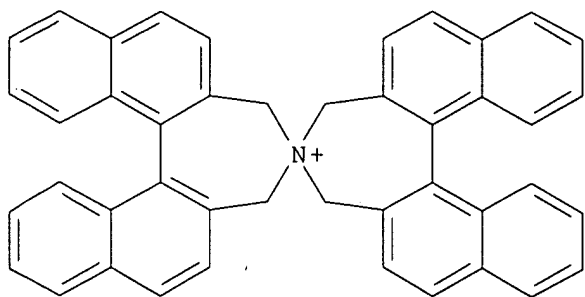
IT 237762-40-2 237762-41-3 237762-42-4  
287384-12-7

RL: CAT (Catalyst use); USES (Uses)

(enantioselective alkylations of glycinate Schiff bases with alkyl  
halides in the presence of chiral binaphthol-derived ammonium salts as  
phase-transfer catalysts)

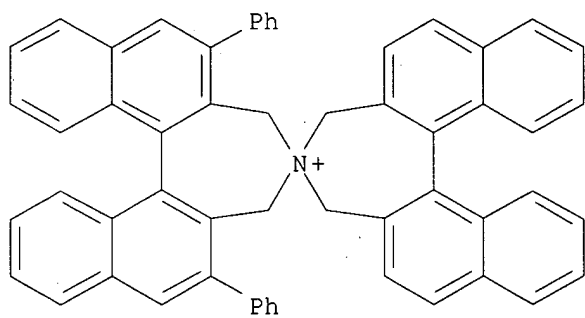
RN 237762-40-2 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-,  
bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



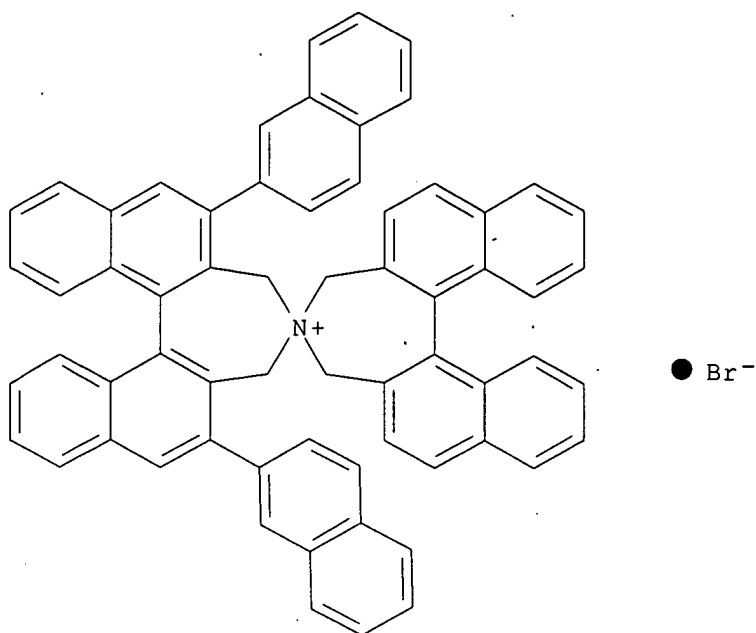
● Br<sup>-</sup>

RN 237762-41-3 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-diphenyl-, bromide, (11bS,11'bs)- (9CI) (CA INDEX NAME)



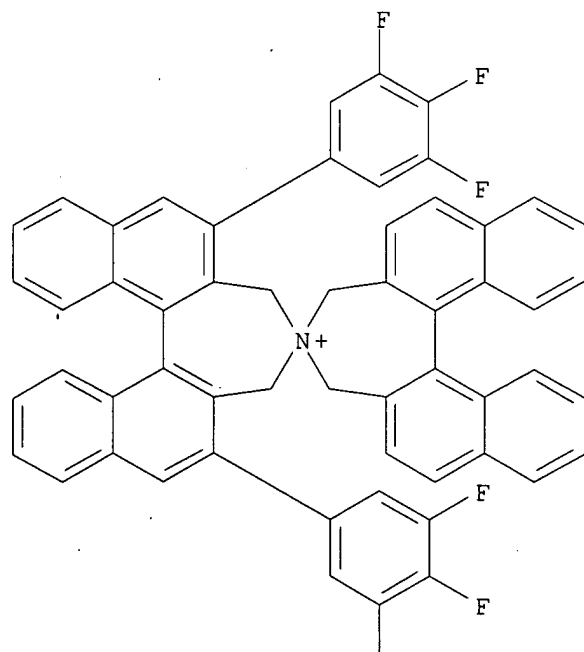
● Br<sup>-</sup>

RN 237762-42-4 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-di-2-naphthalenyl-, bromide (1:1), (11bS,11'bs)- (CA INDEX NAME)



RN 287384-12-7 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)

PAGE 1-A



F

● Br<sup>-</sup>

REFERENCE COUNT: 23 THERE ARE 23 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 72 OF 80, CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2001:669428 CAPLUS

DOCUMENT NUMBER: 135:371970

TITLE: Concise, catalytic asymmetric synthesis of tetrahydroisoquinoline- and dihydroisoquinoline-3-carboxylic acid derivatives

AUTHOR(S): Ooi, Takashi; Takeuchi, Mifune; Maruoka, Keiji  
CORPORATE SOURCE: Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto, 606-8502, Japan

SOURCE: Synthesis (2001), (11), 1716-1718

CODEN: SYNTBF; ISSN: 0039-7881

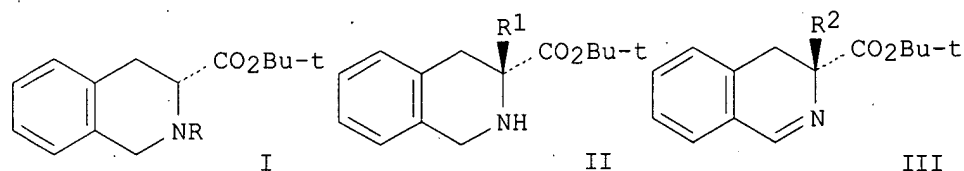
PUBLISHER: Georg Thieme Verlag

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 135:371970

GI



AB Catalytic asym. synthesis of tetrahydroisoquinoline-3-carboxylic acid (Tic) tert-Bu esters I (R = H, C<sub>6</sub>H<sub>5</sub>) has been accomplished by the successful utilization of phase-transfer catalysis of the C2-sym. chiral quaternary ammonium bromides. This approach also enables the facile synthesis of 3-alkylated isoquinolinecarboxylates, tetrahydro derivs. II (R<sub>1</sub> = Me, i-Bu, CH<sub>2</sub>Ph) and dihydro derivs. III (R<sub>2</sub> = Me, CH<sub>2</sub>Ph), with high enantiomeric purities.

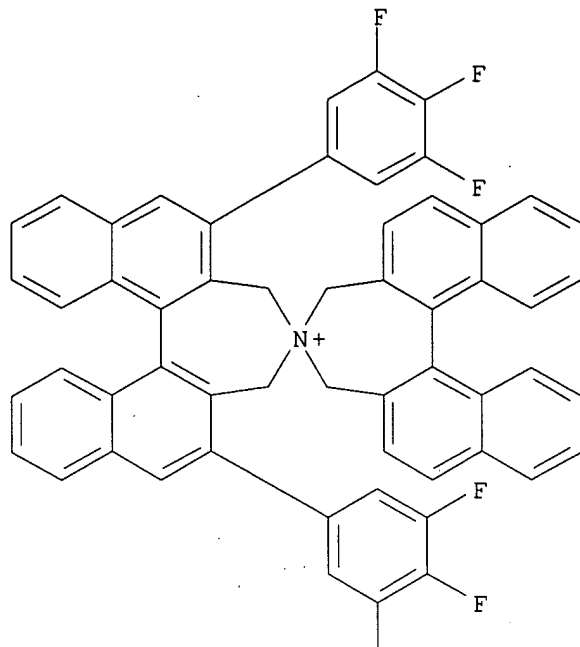
IT 287384-12-7

RL: CAT (Catalyst use); USES (Uses)

(asym. preparation of dihydro- and tetrahydro-isoquinolinecarboxylates in the presence of a chiral quaternary ammonium bromide as a phase transfer catalyst)

RN 287384-12-7 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



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● Br<sup>-</sup>

REFERENCE COUNT: 32 THERE ARE 32 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 73 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2001:508671 CAPLUS

DOCUMENT NUMBER: 135:257431

TITLE: Advantage of anaerobic conditions in the highly

enantioselective synthesis of  $\alpha,\alpha$ -dialkyl-

$\alpha$ -amino acids by chiral phase-transfer catalysis

AUTHOR(S): Ooi, Takashi; Takeuchi, Mifune; Ohara, Daisuke;

Maruoka, Keiji

CORPORATE SOURCE: Department of Chemistry, Graduate School of Science,

Kyoto University, Kyoto, 606-8502, Japan

SOURCE: Synlett (2001), (7), 1185-1187

CODEN: SYNLES; ISSN: 0936-5214

PUBLISHER: Georg Thieme Verlag

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 135:257431

AB Intervention of the enolate oxidation in the catalytic asym. phase-transfer alkylation of protected  $\alpha$ -amino acid derivs. under aerobic conditions has been addressed, and anaerobic conditions have been introduced to obtain synthetically satisfactory chemical yields as well as a high level of enantioselectivity.

IT 287384-12-7

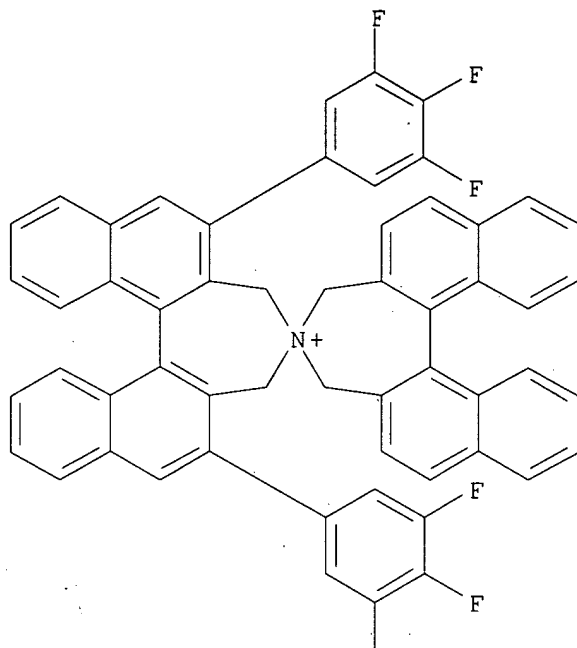
RL: CAT (Catalyst use); USES (Uses)

(preparation of dialkyl amino acids by phase-transfer catalysis under anaerobic conditions with high level of enantioselectivity)

RN 287384-12-7 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)

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REFERENCE COUNT: 13 THERE ARE 13 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 74 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2001:247846 CAPLUS

DOCUMENT NUMBER: 135:45972

TITLE: Asymmetric Alkylation of tert-Butyl Glycinate Schiff Base with Chiral Quaternary Ammonium Salt under Micellar Conditions

AUTHOR(S): Okino, Tomotaka; Takemoto, Yoshiji

CORPORATE SOURCE: Department of Chemistry Graduate School of Pharmaceutical Sciences, Kyoto University, Yoshida Sakyo-ku Kyoto, 606-8501, Japan

SOURCE: Organic Letters (2001), 3(10), 1515-1517  
CODEN: ORLEF7; ISSN: 1523-7060

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal  
LANGUAGE: English  
OTHER SOURCE(S): CASREACT 135:45972

AB The asym. alkylation of the tert-Bu glycinate-benzophenone Schiff base with various arylmethyl bromides catalyzed by O-allyl-N-(9-anthracenylmethyl)cinchonidinium bromide proceeded smoothly under micellar conditions (5 equiv of 1 M KOH and 0.4 equiv of Triton X-100) to give the alkylated products in good yields and with good enantioselectivity (72-85% ee), depending on the electrophiles.

IT 287384-12-7

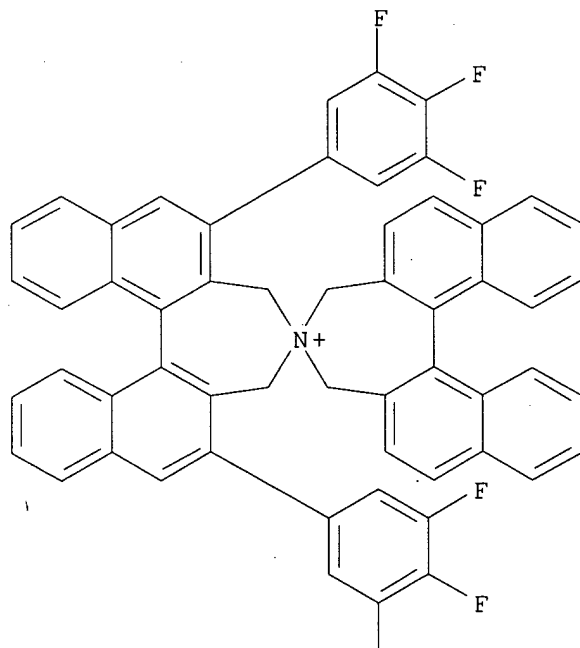
RL: CAT (Catalyst use); USES (Uses)

(asym. alkylation of tert-Bu glycinate Schiff base with chiral quaternary ammonium salt under micellar conditions)

RN 287384-12-7 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)

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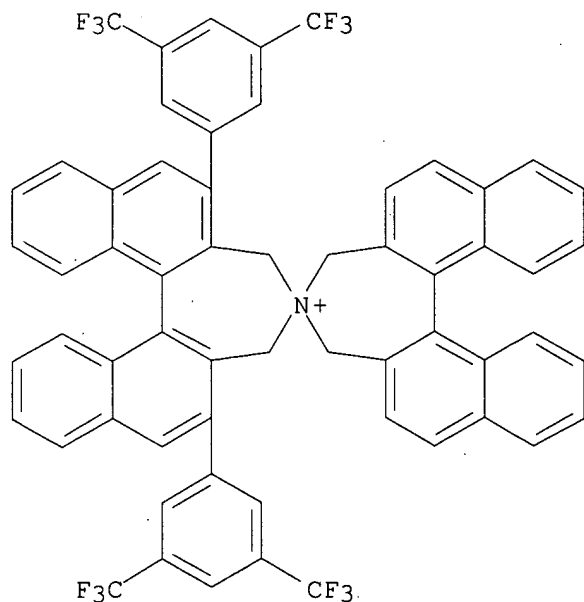
● Br<sup>-</sup>

REFERENCE COUNT: 47 THERE ARE 47 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

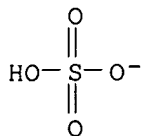
L3 ANSWER 75 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
ACCESSION NUMBER: 2001:247767 CAPLUS  
DOCUMENT NUMBER: 135:45952



TITLE: Distinct Advantage of the in Situ Generation of Quaternary Ammonium Fluorides under Phase-Transfer Conditions toward Catalytic Asymmetric Synthesis  
 AUTHOR(S): Ooi, Takashi; Doda, Kanae; Maruoka, Keiji  
 CORPORATE SOURCE: Department of Chemistry Graduate School of Science, Kyoto University, Sakyo Kyoto, 606-8502, Japan  
 SOURCE: Organic Letters (2001), 3(9), 1273-1276  
 CODEN: ORLEF7; ISSN: 1523-7060  
 PUBLISHER: American Chemical Society  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 OTHER SOURCE(S): CASREACT 135:45952  
 AB Quaternary ammonium fluorides were found to be efficiently generated in situ from ammonium hydrogen sulfates by treatment with com. available potassium fluoride dihydrate (KF·2H<sub>2</sub>O) in THF and were directly used as a fluoride source for the generation of carbon nucleophiles from organosilicon compds. This method can be successfully applied to the preparation of structurally well-defined, C<sub>2</sub>-sym. chiral quaternary ammonium fluorides, thereby allowing catalytic enantioselective Mukaiyama-type aldol reactions under mild conditions.  
 IT 344550-36-3 344550-38-5  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (advantage of in situ generation of quaternary ammonium fluorides under phase-transfer conditions toward catalytic asym. synthesis)  
 RN 344550-36-3 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 2,6-bis[3,5-bis(trifluoromethyl)phenyl]-3,3',5,5'-tetrahydro-, (11bS,11'bS)-, sulfate (1:1) (9CI) (CA INDEX NAME)  
 CM 1  
 CRN 344550-35-2  
 CMF C60 H36 F12 N



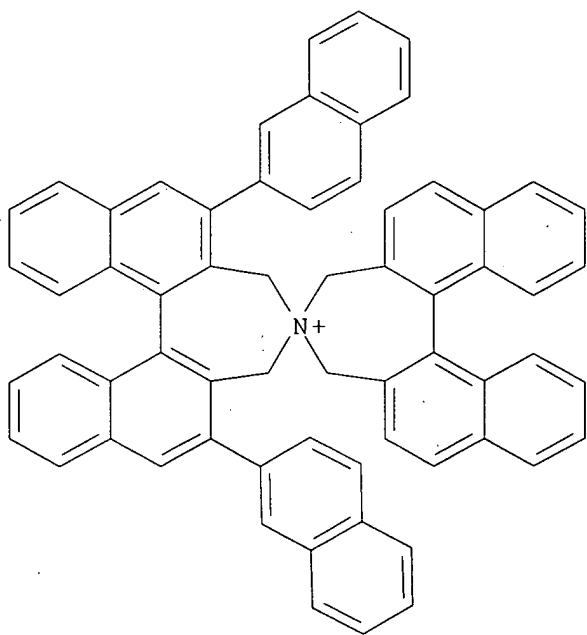
CM 2  
 CRN 14996-02-2  
 CMF H O4 S



RN 344550-38-5 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-di-2-naphthalenyl-, (11bS,11'bS)-, sulfate (1:1) (9CI) (CA INDEX NAME)

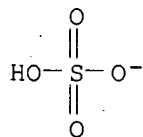
CM 1

CRN 344550-37-4  
 CMF C64 H44 N



CM 2

CRN 14996-02-2  
 CMF H O4 S



REFERENCE COUNT: 29 THERE ARE 29 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 76 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2001:124168 CAPLUS  
 DOCUMENT NUMBER: 134:178476  
 TITLE: Preparation of optically active azepinium compounds

having asymmetric axis and  $\alpha$ -amino acids by using them

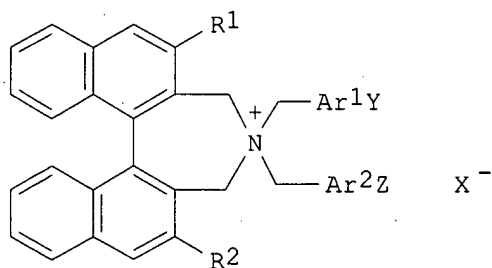
INVENTOR(S): Maruoka, Keiji  
 PATENT ASSIGNEE(S): Nagase and Co., Ltd., Japan  
 SOURCE: Jpn. Kokai Tokkyo Koho, 37 pp.  
 CODEN: JKXXAF

DOCUMENT TYPE: Patent  
 LANGUAGE: Japanese  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 2001048866	A	20010220	JP 2000-121825	20000421
US 6340753	B1	20020122	US 2000-616361	20000713
WO 2001081349	A1	20011101	WO 2001-JP3373	20010419
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW				
RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG				
EP 1277755	A1	20030122	EP 2001-921928	20010419
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR				
US 20020065414	A1	20020530	US 2001-987547	20011115
US 20020103374	A1	20020801	US 2001-987544	20011115
US 6441231	B2	20020827		

PRIORITY APPLN. INFO.: JP 1999-158812 A 19990604  
 JP 2000-121825 A 20000421  
 US 2000-616361 A3 20000713  
 WO 2001-JP3373 W 20010419

OTHER SOURCE(S): CASREACT 134:178476; MARPAT 134:178476  
 GI



AB Title compds. I [R1, R2 = H, C1-6 alkyl, C2-6 alkenyl, C2-6 alkynyl, (un)substituted aralkyl, etc.; Ar1, Ar2 = (un)substituted aryl, heteroaryl, etc.; Y, Z = H, halo, C1-4 alkyl, C1-3 alkoxy, etc.] are prepared R6C:R7NCR5R8CO2R9 [R5 = C1-6 alkyl, (un)substituted C3-9 aryl, aralkyl, etc.; R6, R7 = H, (un)substituted aryl; all of R6-R7 are not H; R8 = H, (un)substituted aryl, aralkyl; R9 = C1-4 alkyl] are stereoselectively prepared by reaction of R6C:R7NCHR8CO2R9 (R6-R9 = same as above) with R5W (R5 = same as above; W = leaving group) in the presence of I as phase-transfer catalysts. (S)-3,5-dihydro-4H-[2,1-c:1',2'-e]azepine was cyclized with (S)-1,1'-bi-2-(bromomethyl)-3-( $\beta$ -naphthyl)naphthyl

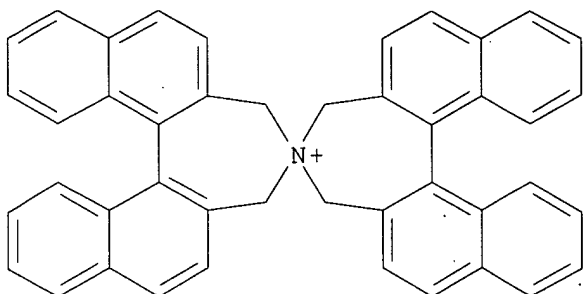
in MeOH in the presence of K<sub>2</sub>CO<sub>3</sub> under reflux for 30 min to give 36% [(S)-3,3'-di(β-naphthyl)-1,1'-binaphthyl-2,2'-dimethylammonium]spiro[(S)-1,1'-binaphthyl-2,2'-dimethylamine] bromide. Reaction of Ph<sub>2</sub>C:NCH<sub>2</sub>CO<sub>2</sub>Bu-tert with PhCH<sub>2</sub>Br in the presence of the compds. prepared above gave 95% (S)-phenylalanine tert-Bu ester benzophenone Schiff base.

IT 237762-40-2P 237762-41-3P 237762-42-4P  
287384-12-7P

RL: CAT (Catalyst use); IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
(preparation of optically active azepinium compds. as alkylation catalyst for preparing amino acids)

RN 237762-40-2 CAPLUS

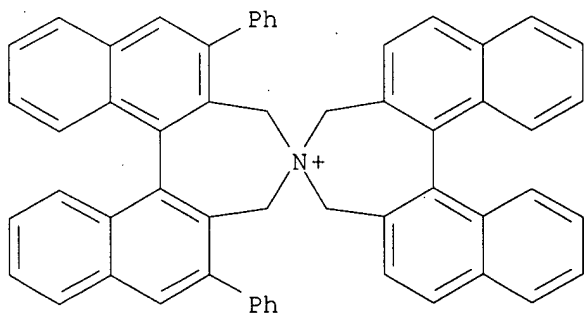
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



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RN 237762-41-3 CAPLUS

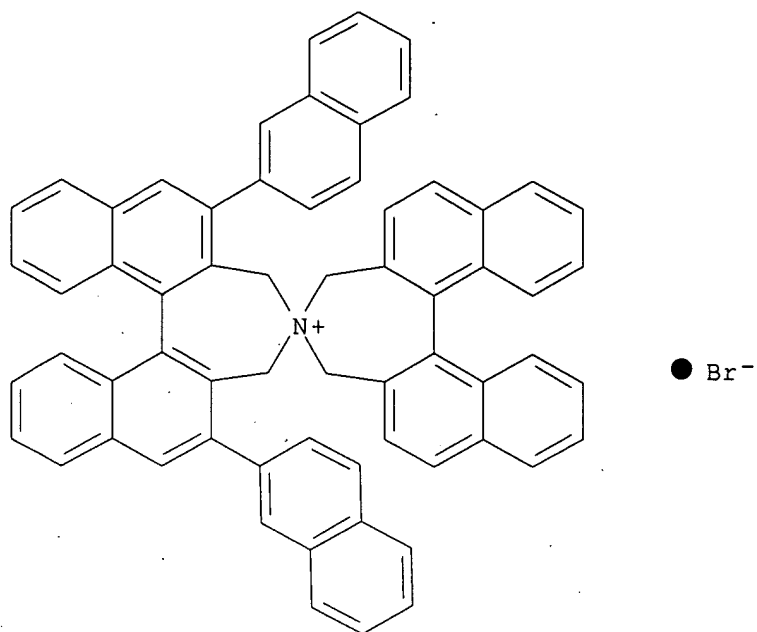
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-diphenyl-, bromide, (11bS,11'bS)- (9CI) (CA INDEX NAME)



● Br<sup>-</sup>

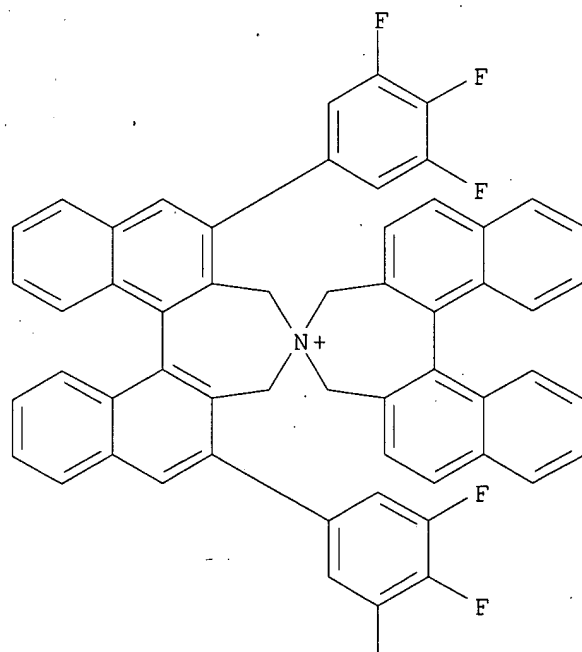
RN 237762-42-4 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-di-2-naphthalenyl-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



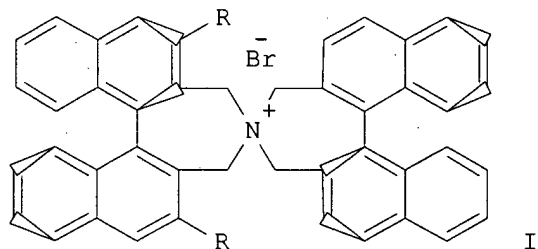
RN 287384-12-7 CAPLUS  
 CN 4,4'-Spiro[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)

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F● Br<sup>-</sup>

L3 ANSWER 77 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2000:833970 CAPLUS  
 DOCUMENT NUMBER: 134:71862  
 TITLE: Facile synthesis of L-Dopa tert-butyl ester by  
 catalytic enantioselective phase-transfer alkylation  
 AUTHOR(S): Ooi, Takashi; Kameda, Minoru; Tannai, Hidenori;  
 Maruoka, Keiji  
 CORPORATE SOURCE: Department of Chemistry, Graduate School of Science,  
 Kyoto University, Kyoto, 606-8502, Japan  
 SOURCE: Tetrahedron Letters (2000), 41(43), 8339-8342  
 CODEN: TELEAY; ISSN: 0040-4039  
 PUBLISHER: Elsevier Science Ltd.  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 OTHER SOURCE(S): CASREACT 134:71862  
 GI

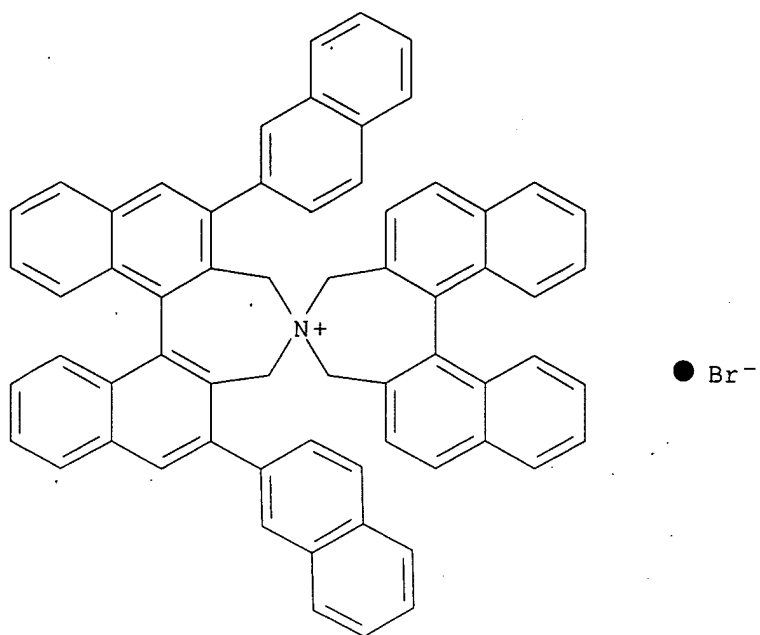


AB Facile synthesis of tert-Bu esters of L-Dopa and of L-tyrosine has been achieved by using C2-sym. chiral quaternary ammonium salts I (R =  $\beta$ -naphthyl, 3,4,5-trifluorophenyl) as phase-transfer catalysts for the asym. alkylation of glycinate Schiff base, Ph<sub>2</sub>C:NCH<sub>2</sub>CO<sub>2</sub>Bu-t, with 3,4-di(benzyloxy)benzyl bromide and 4-(benzyloxy)benzyl bromide, resp. The "scale-up" experiment performed with 5.00 g of glycinate Schiff base represents the practical aspect of this approach.

IT 237762-42-4 287384-12-7  
 RL: CAT (Catalyst use); USES (Uses)  
 (facile preps. of L-Dopa and tyrosine tert-Bu esters by catalytic, asym. phase-transfer alkylation of glycinate Schiff base)

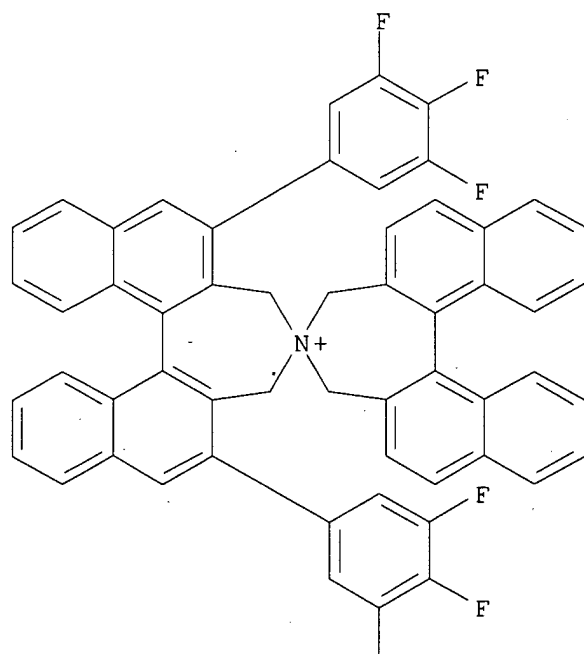
RN 237762-42-4 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-di-2-naphthalenyl-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



RN 287384-12-7 CAPLUS  
 CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
 2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bS)- (CA INDEX  
 NAME)

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REFERENCE COUNT: 9 THERE ARE 9 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 78 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2000:737803 CAPLUS

DOCUMENT NUMBER: 134:29004

TITLE: Dramatic rate enhancement by ultrasonic irradiation in liquid-liquid phase-transfer catalytic reactions

AUTHOR(S): Ooi, Takashi; Tayama, Eiji; Doda, Kanae; Takeuchi, Mifune; Maruoka, Keiji

CORPORATE SOURCE: Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto, 606-8502, Japan

SOURCE: Synlett (2000), (10), 1500-1502

CODEN: SYNLES; ISSN: 0936-5214

PUBLISHER: Georg Thieme Verlag

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 134:29004

AB Significant rate enhancement was observed in liquid-liquid phase-transfer catalytic epoxidn. and alkylation under ultrasonic irradiation Its advantage was also demonstrated in the asym. alkylation of tert-Bu glycinate-benzophenone Schiff base using C2-sym. chiral phase-transfer catalyst.

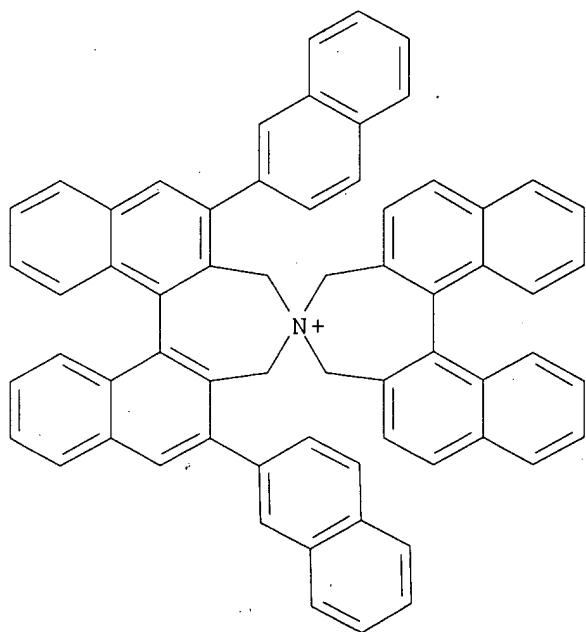
IT 237762-42-4

RL: CAT (Catalyst use); USES (Uses)

(ultrasound-enhanced liquid-liquid phase-transfer catalytic reactions)

RN 237762-42-4 CAPLUS

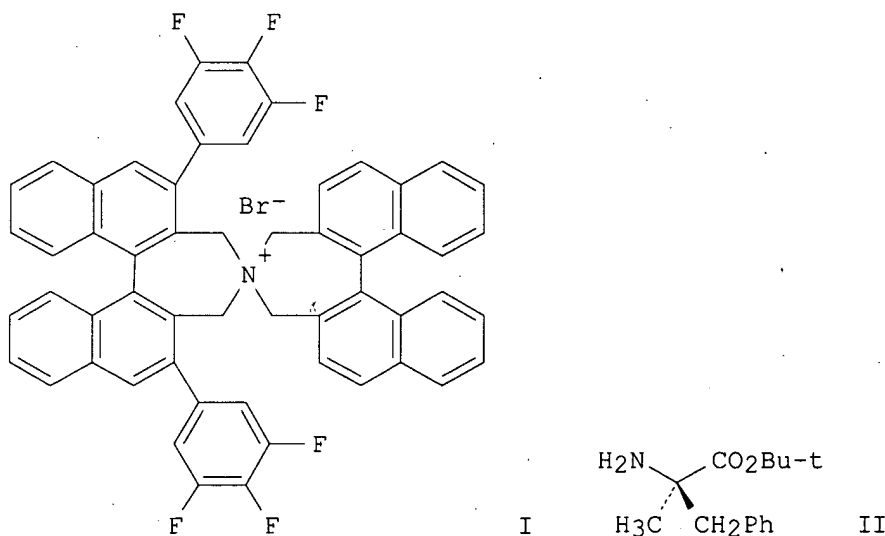
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-di-2-naphthalenyl-, bromide (1:1), (11bS,11'bs)- (CA INDEX NAME)

● Br<sup>-</sup>



REFERENCE COUNT: 26 THERE ARE 26 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 79 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN  
ACCESSION NUMBER: 2000:316253 CAPLUS  
DOCUMENT NUMBER: 133:150858  
TITLE: Practical catalytic enantioselective synthesis of  $\alpha,\alpha$ -dialkyl- $\alpha$ -amino acids by chiral phase-transfer catalysis  
AUTHOR(S): Ooi, Takashi; Takeuchi, Mifune; Kameda, Minoru; Maruoka, Keiji  
CORPORATE SOURCE: Department of Chemistry Graduate School of Science, Hokkaido University, Sapporo, 060-0810, Japan  
SOURCE: Journal of the American Chemical Society (2000), 122(21), 5228-5229  
CODEN: JACSAT; ISSN: 0002-7863  
PUBLISHER: American Chemical Society  
DOCUMENT TYPE: Journal  
LANGUAGE: English  
OTHER SOURCE(S): CASREACT 133:150858  
GI



AB The authors devised a broadly useful procedure for the asym. synthesis of a wide variety of  $\alpha,\alpha$ -dialkyl- $\alpha$ -amino acids based on the highly enantioselective solid-liquid phase transfer catalytic alkylation of aldimine Schiff base of amino acid tert-Bu esters using structurally well-defined C2-sym. chiral quaternary ammonium bromides. For example, DL-4-ClC6H4CH:NCH(Me)CO<sub>2</sub>Bu-t was alkylated by PhCH<sub>2</sub>Br in the presence of chiral phase transfer catalyst I in toluene, followed by treatment with citric acid in THF, to afford the alkylated D-amino acid II in 85% yield with 98% enantiomeric excess.

IT 287384-12-7

RL: CAT (Catalyst use); USES (Uses)

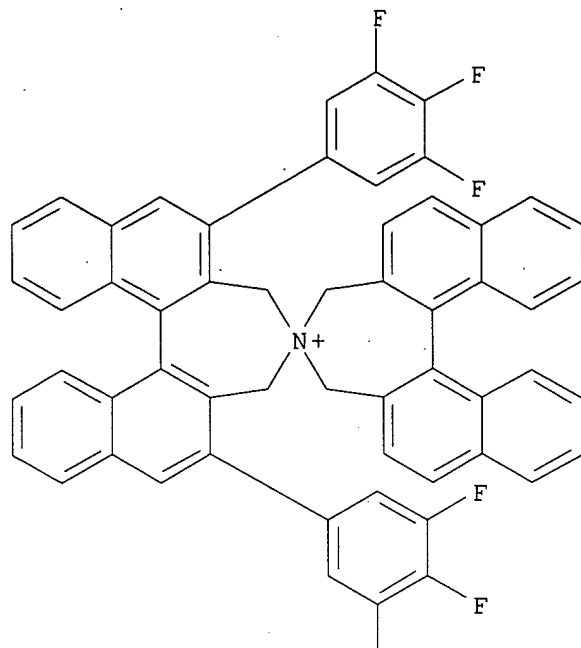
(efficient catalyst; preparation of  $\alpha,\alpha$ -dialkyl- $\alpha$ -amino acids via enantioselective alkylation of amino acid Schiff bases in the presence of chiral phase-transfer catalysts)

RN 287384-12-7 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-bis(3,4,5-trifluorophenyl)-, bromide (1:1), (11bS,11'bS)- (CA INDEX

NAME)

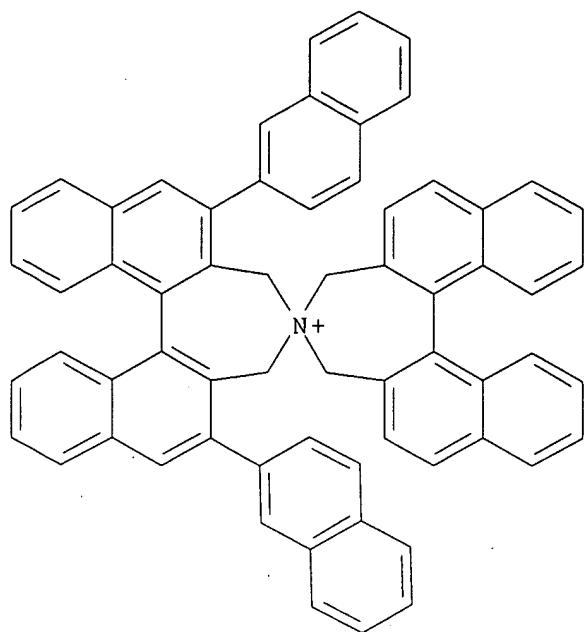
PAGE 1-A



PAGE 2-A



IT 237762-42-4  
RL: CAT (Catalyst use); USES (Uses)  
(poor catalyst; preparation of  $\alpha,\alpha$ -dialkyl- $\alpha$ -amino acids  
via enantioselective alkylation of amino acid Schiff bases in the  
presence of chiral phase-transfer catalysts)  
RN 237762-42-4 CAPLUS  
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-  
2,6-di-2-naphthalenyl-, bromide (1:1), (11bS,11'bs)- (CA INDEX NAME)



● Br<sup>-</sup>

REFERENCE COUNT: 28 THERE ARE 28 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 80 OF 80 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1999:436506 CAPLUS

DOCUMENT NUMBER: 131:157942

TITLE: Molecular Design of a C<sub>2</sub>-Symmetric Chiral Phase-Transfer Catalyst for Practical Asymmetric Synthesis of α-Amino Acids

AUTHOR(S): Ooi, Takashi; Kameda, Minoru; Maruoka, Keiji  
CORPORATE SOURCE: Department of Chemistry Graduate School of Science, Hokkaido University, Sapporo, 060-0810, Japan

SOURCE: Journal of the American Chemical Society (1999), 121(27), 6519-6520

CODEN: JACSAT; ISSN: 0002-7863

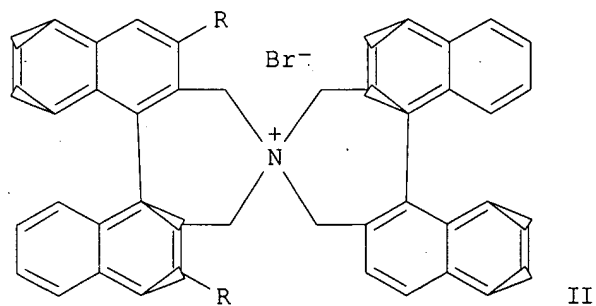
PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 131:157942

GI



II

AB The authors report the synthesis of a C<sub>2</sub>-sym. chiral quaternary ammonium salt and its successful application in a highly efficient enantioselective

alkylation of tert-Bu glycinate-benzophenone Schiff base (I) under mild phase-transfer conditions. Structurally more rigid chiral spiro ammonium salts [(II); R = H, Ph, 2-naphthyl] were synthesized and used. Catalyst II (R = 2-naphthyl) gave enantio-selectivities generally exceeding 90% ee for alkylation of I with a variety of alkyl halides.

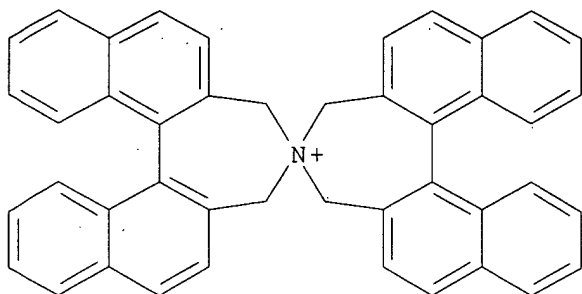
IT 237762-40-2P 237762-41-3P 237762-42-4P

RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)

(preparation of as C2-sym. chiral phase-transfer catalyst for practical asym. synthesis of  $\alpha$ -amino acids)

RN 237762-40-2 CAPLUS

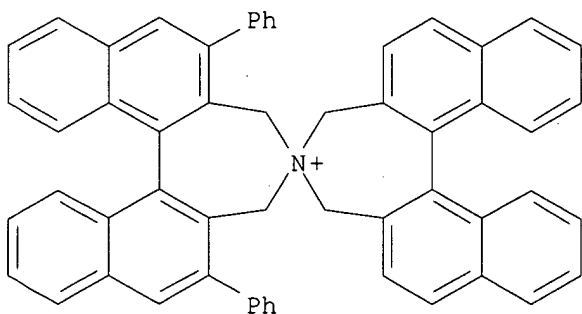
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



● Br<sup>-</sup>

RN 237762-41-3 CAPLUS

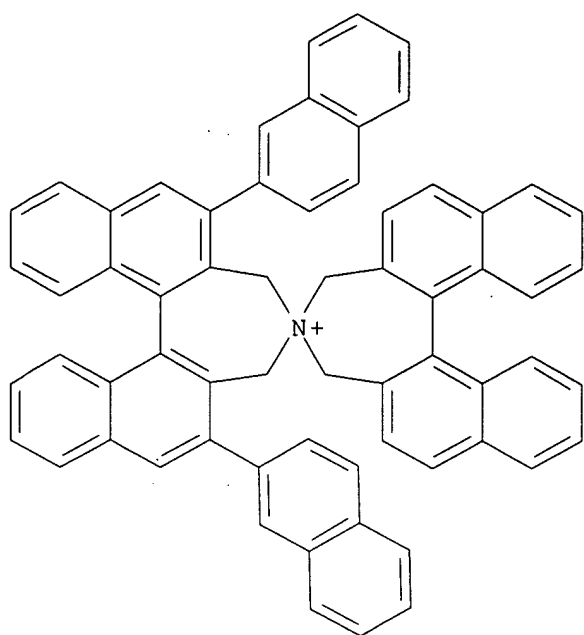
CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-diphenyl-, bromide, (11bS,11'bS)- (9CI) (CA INDEX NAME)



● Br<sup>-</sup>

RN 237762-42-4 CAPLUS

CN 4,4'-Spirobi[4H-dinaphth[2,1-c:1',2'-e]azepinium], 3,3',5,5'-tetrahydro-2,6-di-2-naphthalenyl-, bromide (1:1), (11bS,11'bS)- (CA INDEX NAME)



REFERENCE COUNT:

24

THERE ARE 24 CITED REFERENCES AVAILABLE FOR THIS  
RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT